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14. ABSTRACT

The concept of ionic liquids, formed by proton transfer from Bronsted acid to Bronsted base, serving as the proton transport media in fuel cells is evaluated at several levels. Firstly a wide range of protic ionic liquids formed from acids of a wide range of acid strengths to a variety of nitrogenic bases of different base strengths, nearly 100 in all, has been synthesized and characterized. A proton free energy level diagram, based on aqueous solution pKa data, has been developed to permit predictions of the properties of arbitrarily chosen acid-base pairs, and a modified glass electrode to directly study the proton transfer energetics, has been developed. Secondly, a class of siloxane polymers with pendant amine, or alternatively,

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Fuel cells using the protic ionic liquid and rotator phase solid electrolyte principles

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The concept of ionic liquids, formed by proton transfer from Bronsted acid to Bronsted base, serving as the proton transport media in fuel cells is evaluated at several levels. Firstly a wide range of protic ionic liquids formed from acids of a wide range of acid strengths to a variety of nitrogenic bases of different base strengths, nearly 100 in all, has been synthesized and characterized. A proton free energy level diagram, based on aqueous solution pKa data, has been developed to permit predictions of the properties of arbitrarily chosen acid-base pairs, and a modified glass electrode to directly study the proton transfer energetics, has been developed. Secondly, a class of siloxane polymers with pendant amine, or alternatively, pendant sulfonic acid groups, has been synthesized, and polymeric salts formed by neutralizing the pendant groups with acids or bases respectively have been formed and characterized. Their ability to imbibe the ionic liquids without loss of mechanical strength has been tested and conductivities up to 10mS/cm, at 100ºC, has been evaluated. Finally, the assembly of gas diffusion fuel cells running at up to 150ºC, using either the PILs or the PIL-swollen membrane as the electrolyte, has been undertaken.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. Highly decoupled ionic and protonic solid electrolyte systems, in relation to other relaxing systems and their energy landscapes". F. Mizuno*#, J.-P Belieres*, N. Kuwata@$, A. Pradel@, M. Ribes@, and C. A. Angell*, J. Non-Cryst. Solids, 352 (42-49): 5147-5155 (2006)

2.Binary Inorganic salt mixtures as high conductivity electrolytes for >100ºC fuel cells J.-P. Belieres, D. Gervasio, and C. A. Angell, Chem. Commun. 2006, DOI: 10.1039/b611150e

3.Protic ionic liquids: Preparation, characterization , and the proton transfer energy level diagram.. (invited for special issue on Ionic Liquids. J.-P. Beleieres and C. A. Angell, J. Phys. Chem. B, 111 (18), 4926 -4937 (2007)

4. Parallel developments in inorganic, aprotic, and protic ionic liquids: physical chemistry and applications" C. Austen Angell, Nolene Byrne and Jean-Philippe Belieres, Accounts of Chemical Research (special issue on Ionic Liquids) 40, 1228-1236, (2007)

Number of Papers published in peer-reviewed journals: 4.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

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(c) Presentations

1. Opening talk at COIL II (2nd. International conference on Ionic Liquids.
C. A. Angell, N. Byrne, J-P. Belieres, "Proton activity in ionic liquids: The ILPA index and its application in optimizing fuel cell efficiency, protein stability, and large molecule solubility". Yokohama, Japan, August 5th, 2007

2. Plenary talk at 16th Solid State Ionics conference (SSI-16) Shanghai, China, July 1-6 (2007) C. A. Angell. "On the relation of "dry" proton to "fast" Li+ conductivity in crystalline, glassy and polymer solid electrolytes,"

3. Invited Talk "Protic Salt Polymer Membranes: Water-Free Proton-Conducting Membranes", Southeast Regional Meeting American Chemical Society (SERMACS), Greenville, SC, October 26, 2007.

4. Invited talk "Fuel Cells for Clean Power and Energy", Korean Electrochemical Society, Seoul Korea, Friday October 5, 2007.

5. Invited Talk "Protic Salt Polymer Membranes: High-Temperature Water-Free Proton-Conducting Membranes", FreedomCar Fuel Cell Tech Team (GM, Ford, Chrysler, DoE), Detroit, MI June 20, 2007.

6. Invited Talk "High temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFCs) for Portable Power in Large-Scale Energy Storage Devices", Paper Number 195, 212th Meeting of the Electrochemical Society, Washington DC, October 11, 2007.

7. Invited Talk "Proton transfer salts: A new class of solvent-free, involatile, fuel cell electrolytes", D. F. Gervasio, J-P Belieres, and C. Austen Angell, paper number 171, presented to American Chemical Society, Division of Fuel Chemistry, Fuel Cell Chemistry and Operation, San Francisco, CA, September (2006).

8. Invited Talk "Proton Transfer Salts: a New Class of Solvent-free, Involatile, Fuel Cell Electrolytes", Don Gervasio (speaker), Jean-Philippe Belieres, C. Austen Angell, H. Markusson (Chalmers University of Technology), and W. Xu (Ferro Corporation), Electrochemical Society, 2nd International Conference on Polymer Batteries and Fuel Cells, Riviera Hotel, Las Vegas, Nevada, USA Ex. Abstract No. 205 (2005).

9. Jean-Philippe Belieres, Xiao-Guang Sun, Don Gervasio and C. Austen Angell, Ionic liquids and fuel cell membranes: a new generation of polymer electrolyte fuel cell membranes using the anhydrous protic ionic liquid principle, PIRA conference on Ionic Liquids, Orlando, FL, December 11-13, 2006

10. J.-P. Belieres, N. Byrne, X. Sun, D. Gervasio, J. Yarger and C. A. Angell, Binary inorganic salt mixtures as high conductivity liquid electrolytes for high temperature fuel cells, Division B2 - Advanced Materials for Fuel Cells and Batteries - Abstract #321, The Electrochemical Society, Chicago, IL, May 6-10, 200711.   J.-P.

11. Belieres, N. Byrne, D. Gervasio, C. A. Angell, Protic ionic liquids and the PEM fuel cell, 2nd International Congress on Ionic Liquids, poster session, #3P07-081, Yokohama, Japan, August 5-10, 2007

12. Xiao-Guang Sun, Jean-Philippe Belieres, Don Gervasio, C. Austen Angell, Development of materials having high ionic conductivities for high temperature fuel cell applications, The 208th Meeting of The Electrochemical Society, Los Angeles, CA, Oct. 16-21, 2005, Abs. #928.

13.Xiao-Guang Sun, Don Gervasio, C. Austen Angell, High temperature fuel cells using ionic polysiloxane membranes, with and without ionic plasticizers, The 213th Meeting of The Electrochemical Society, Phoenix, AZ, May. 18-22, 2008, Abs. #442.

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Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED	
Jean-Philippe Belieres	0.50	
FTE Equivalent:	**0.50**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED	
Xiao-Guang Sun	1.00	
Jean-Philippe Belieres	0.40	
FTE Equivalent:	**1.40**	
Total Number:	**2**	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Don Gervasio	0.00	No
Charles Austen Angell	0.00	No
FTE Equivalent:	**0.00**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics
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The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:······ 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:······ 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Jean-Philippe Belieres

Total Number: **1**

Names of other research staff

NAME   PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

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5   **Ionic liquids & Ionic liquid acids with high temperature stability for fuel cell and other high**

Patent Filed in US? (5d-1)   Y

Patent Filed in Foreign Countries? (5d-2)   Y

Was the assignment forwarded to the contracting officer? (5e)   N

Foreign Countries of application (5g-2):

     5a: Charles Austen Angell

   5f-1a: Arizona State University

    5f-c: 2122 S Paseo Loma

        Mesa   AZ   85287

     5a: Wu Xu

   5f-1a: Arizona State University

    5f-c: c/o C. A. Angell, 2122 S.Paseo Loma

        Mesa   AZ   85287

     5a: Jean-Philippe Belieres

   5f-1a: Arizona State University

    5f-c: c/o C. A. Angell, 2122 S.Paseo Loma

        Mesa   AZ   85287

     5a: Masahiro Yoshizawa

   5f-1a: Arizona State University

    5f-c: c/o C. A. Angell, 2122 S.Paseo Loma

        Mesa   AZ   85287

Fuel cells using the protic ionic liquid and rotator phase solid electrolyte principles:

A final Report

C. Austen. Angell and Don Gervasio,
Arizona State University,
Tempe, AZ

TABLE OF CONTENTS

A. OBJECT OF THE RESEARCH

This research program has been developed to follow up on the concern that fuel cell research has to date been largely and unnecessarily focused on the use of aqueous electrolytes as the proton carriers between hydrogen anode and oxygen cathode. Water has been either the base which accepts the proton in acid electrolyte cells, like the Nafion based cell, or the acid which donates the proton in the Bacon-type alkaline fuel cell.

In our initial studies of ionic liquids(*1-5*), we stumbled across the idea that the protonated amine bases of classical proton transfer salts, in the cases where these existed as ambient temperature ionic liquids, could equally well serve as the proton carriers, and while we were attempting to verify that our favorable results were not artifactual, there appeared the first announcement that this idea was valid, in the form of the Chemical Communication from the Watanabe laboratory in Japan. It is with the follow-up of these developments, under a research program supported by the ARO, that this final report is concerned.

B. BACKGROUND TO THE RESEARCH

As our understanding of this subject advances we recognize that electrolytes of this type, electrolytes that lack any free solvent, were actually studied quite a long time ago, utilizing as protic cation either the hydronium ion H_3O^+ in the ionic liquid H_3O^+ $CF_3SO_3^-$ (*6*) or the phosphoric acid cation $H_4PO_4^+$ protonated by triflic acid(*7*). However, the use of nitrogenous bases as the proton carrier in fuel cells seems to have begun only recently, beginning with Kreuer's studies(*8*) of imidazole protonated by sulfuric acid and imidazole incorporated in polymer membranes (*9*) with pendant acid groups. In these cases, though, there was always excess imidazole present in the expectation that the proton flow could become Grotthus-like. Kreuer's work, though pioneering in this respect, has not lead to a good fuel cell because the conductivities that their membranes could provide was not very high.

Much more successful have been the phosphoric acid cells in which the electrolyte conductivity is high thanks to a genuine "free" proton (sometimes called "dry" proton) contribution to the conductivity(*10*). As is seen in Fig. 1, however, the output voltage for phosphoric acid cells is limited (due apparently to absorption of phosphate on the platinum surface (*11*). These cells have been considered by many to be unacceptable for long term applications because of liquid electrolyte leaking between cells in a stack and causing an "ionic short", though cells based on polyimidazole-H_3PO_4 composites(*12*) with a special morphology that prevents H_3PO_4 flow, but not H^+ flow(*13*), have been demonstrated in 15,000 hr tests by Benicewicz and associates (*14*), and are now in commercial production.

There have been other reports of fuel cells based on the use of the *aprotic* ionic liquids as electrolytes. For instance de Souza and co-workers (*15*) report high electrochemical efficiencies from a cell utilizing butylethylimidazolium BF_4^- as electrolyte, but do not address the question of how protons are moving through such a cell. Hagiwara and coworkers (*16*), on the other hand, used a similar cation 1-ethyl-3-methyl imidazolium with the hydrogen-incorporating anion HF_2^-, though with extra HF molecules to solvate it, and obtained voltage-current curves which appear to be

comparable with those of Fig. 1 (though the figures differ in orientation and show current in unexplained units of negative mA. The open circuit voltage was in this case quite high and stable, though dropped rapidly under current load, as in Fig. 1 (a).

Finally, Sekhon et al(*17*) have reported the incorporation of triflic acid into ionic liquid swollen polyvinylidinenedifluoride - hexafluoropropylene co-polymer that was used for Li conducting electrolyte preparation in prior years. The acid-plasticized polymer was further plasticized with propylene carbonate to boost its conductivity to an acceptable level. The incorporation of excess acid in an ionic liquid is analogous to the case of the acid fluoride electrolyte of Hagiwara et al.(*16*) The membrane was shown capable of producing current in a gas diffusion cell such as that used in our own work discussed below.

There has, overall, been strangely little follow-up of Susan et al's initial paper, though some additional work from the same group has recently (2007) appeared, using again butylimidazolium cation and TFSI$^-$ anions, both at stoichiometric protic salt composition and with excess base. The best performance was obtained with the stoichiometric salt, notwithstanding the higher conductivity of the base-enriched electrolyte. Comparison was also made with H_3PO_4 as electrolyte, although the authors describe the latter as "anhydrous" in which case the performance is guaranteed to be relatively poor (best performance is obtained (at 160ºC) with a water loading of 16 wt *%* corresponding to one water per dihydrogenphosphate anion.

While there has been little work on actual fuel cells reported, there have been a number of reports on the fabrication of membranes that might be used in fuel cells. A good example is the. type Again these have mostly involved the incorporation of anhydrous aprotic ionic liquids into polymers of different types for instance, the work of Doyle and co-workers on incorporation of ethylmethylimadazolium tetrafluoroborate into Nafion polymers(*18*). There is, however, one 2006 report from the group of Jim Kinder at NASA GLENN laboratories, where our co-worker J.-P. Belieres (see Results and Publications) worked over the summer of 2004. Belieres worked on the (ASU-patented) idea of incorporating **protic** ionic liquids into polymer membranes to make proton-transporting components for fuel cells exhibiting small cathode overpotentials. Tigelaar, Kinder, et al(*19*) now report the successful testing of this idea using the Watanabe salts (which are contra-indicated in our own work) imidazolium bisulfate, triflate and TFSI. They made the interesting observation that the amount of salt that was imbibed by the polymer depended on a synergism between anion and polymer, i.e. differed substantially from polymer to polymer for a given salt. They also noted that the salts were much more readily imbibed by their rodlike polyphenyl pyridinium polymer than by the more flexible Nafion membranes.

These authors reported 100ºC conductivities, 10^{-2} Scm^{-1}, that are almost as high as those reported in our work (see section B where a graphical comparison with our work will be given). With the incorporation of our inorganic salt eutectics (ref. (*20*) and Figs. 6-8) these polymers may perform very well in fuel cells.

In our own program, following our initial encouraging demonstration of low overvoltage current flow(*4*) the research has proceeded on three main fronts - synthesis of ionic liquids, testing performance in liquid electrolyte fuel cells, and synthesis of polymer hosts imbibers for ionic liquids. There have also been studies of novel characterization

instrumentation, and of possible solid state electrolytes as summarized in the following section.

C. RESULTS OF RESEARCH IN THIS LABORATORY

We present a broad account of our research accomplishments under this grant below, but first give a summary of their most exciting aspects.

SYNOPSIS

1. *Protic Ionic Liquids.* We have synthesized and characterized over 100 distinct proton transfer salts, the majority of which are liquid below 100ºC hence qualify as ionic liquids. We have devised **an energy level diagram,** (analogous to redox energy level diagram**,** but for protons rather than electrons**)** to describe their stabilities in terms of the free energy of the proton transfer process by means of which they were formed. This energy level scheme allows us to predict the stabilities of the ionic liquid formed by any combination of acid and base which appears on the diagram. Many ionic liquid properties are determined by this transfer energy, so the diagram is predictive.

2. *Fuel cells.* We have used many ionic liquids from the above compilation in H_2/O_2 fuel cells and have determined that there is some correlation, in the cell open circuit voltage, with the proton transfer energy. This maximizes at the theoretical value for an intermeditate range of transfer energies. In some cells this voltage can be maintained during current load, in a very promising manner. However, the electrowetting phenomenon prevents proper evaluation of high load behavior. This should be overcome with good membrane assemblies, discussed next. In a recent development, that has won some publicity, we discovered that inorganic protic salts can be used as electrolytes and in some cases hold promise of outperforming the phosphoric acid cell at high loads as well as low.

3. *Membranes with good mechanical properties and high conductivities.* We have synthesized anionic and cationic siloxane chain and crosslinked membranes which can serve both as dry polymers for cells, and as the base for imbibing of the above ionic liquids ("wet" membranes). The plasticized (wet) membranes have much greater membrane conductances. We have also produced a variety of other cationic membranes, and characterized their (less satisfactory) conductivities.

4. *Solid state ion conductors with high conductivity, partially by "dry" protons.* We have identified certain crystalline systems with melting points above 100ºC in which the conductivity is very high, and in which the diffusivity of protons associated with anionic groups is much higher than for other protons in the system, possibly due to a Grotthus type transport mechanism

5. ***Glass electrode for ionic liquid proton activity measurements..*** We have designed (and patented) a glass electrode for the study of the effective pH of protic ionic liquids and have shown that the effective pH can be calibrated and correlated with directly measured NMR proton chemical shifts. The preparation of buffered solutions has been worked out. The new pH meter can also be used to obtain, by electrochemical measurements, the differences in free energy between aqueous solutions and protic ionic liquid systems of equal "effective pH". The equilibration time for such pH measurements is surprisingly not much longer than that for aqueous solutions.

Detailed review of Research Findings.

1. Protic ionic Liquids, and the proton energy level diagram.
The main findings from this detailed study are contained in the major manuscript 'Preparation and characterization of new protic ionic liquids, and the proton transfer free energy level diagram(*21*), which is submitted with this proposal as supplementary material. There are also three other more general papers on the subject which were solicited for various books and meetings. These are reported in the section on publications from the grant. For those cases where the proton energy "gap" is not too large a "boiling" phenomenon, in which the total vapor pressure established by the original molecular acid and base (due to thermally induced back transfer of the proton) exceeds I atm pressure, can be observed. This boiling point can be compared with that expected from the component molecular liquids behaving as non-reactive ideal solutions, and an "excess boiling point" can be obtained which is a consequence of the lowering of the vapor pressure due to the proton transfer to form ions.

Not surprisingly this "excess boiling temperature' proves to be related to the energy of the proton transfer, which is at this point best assessed from the difference in pKa values of the acid and base. The correlation is shown in Fig. 3.
However, since this latter quantity is determined in aqueous solution, the proton transfer energy obtained in this manner cannot be expected to be accurate. This is discussed in the J. Phys. Chem. paper (Supp. Matt), where an alternative method obtaining the transfer energy from the free energies of formation of the neat salt and the two neat reactants is described. Although not available for many cases, this number allows for an estimate of the error involved in the use of the (generally available) ΔpK_a values. It amounts to about 30% per mole which is quite large though is probably fairly uniform across the board, such that absolute values are effected more than the relative ones. In part 5 below we discuss progress towards obtaining direct measures of this proton transfer free energy.
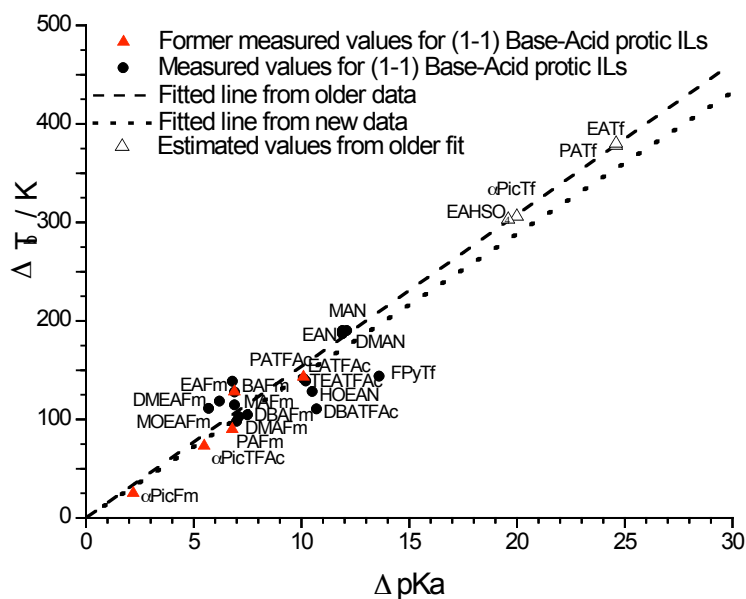
Figure. 3. Excess boiling point for various PILs showing correlation with proton transfer energy"gap".

The presence of this uncertainty has lead us to propose a novel device for obtaining data that will be much more reliable since the data are now obtained from measurements made in the absence of water. It is discussed further in section 5 below. In the absence of direct data, we constructed a proton free energy level diagram for individual acid/conjugate base couples based on the concepts of physicist Ronald Gurney as developed in his classic book "Ionic Processes in Solution".

An extended version of this basic diagram, one which includes very strong acids far above, and very strong bases far below, the limits of Fig. 4, is shown in the Supp. Matt. J. Phys. Chem. paper where it is used to emphasize the difference between the acidic and basic electrolytes of ordinary aqueous electrolyte solutions (in which water acts as the base and as the acid, respectively) and the protic ionic liquids. This is a much broader field of acids and bases in which any one of the molecules in the right hand column can act as the base for a class of proton transfer salts in which the cation is determined by the chosen base, and anion is determined by the acid that transfers its proton. If the base has a high pKa value then the salt will be acid, for example, hydronium triflate, If it is a stronger base like ammonia or ethylamine, then the salt will be more neutral.
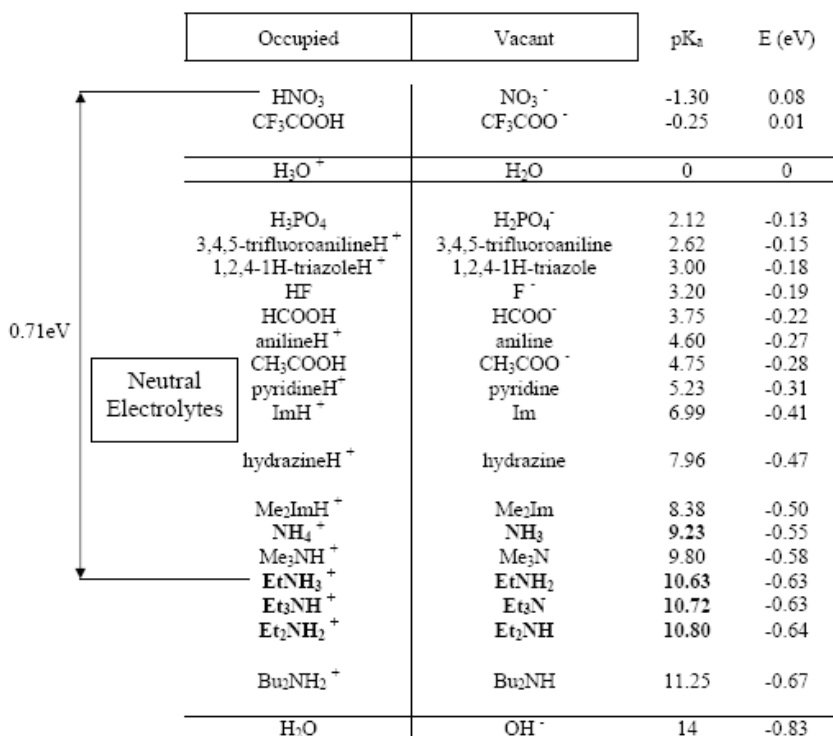
Occupied	Vacant	pK$_a$	E (eV)
HNO$_3$	NO$_3^-$	-1.30	0.08
CF$_3$COOH	CF$_3$COO$^-$	-0.25	0.01
H$_3$O$^+$	H$_2$O	0	0
H$_3$PO$_4$	H$_2$PO$_4^-$	2.12	-0.13
3,4,5-trifluoroanilineH$^+$	3,4,5-trifluoroaniline	2.62	-0.15
1,2,4-1H-triazoleH$^+$	1,2,4-1H-triazole	3.00	-0.18
HF	F$^-$	3.20	-0.19
HCOOH	HCOO$^-$	3.75	-0.22
anilineH$^+$	aniline	4.60	-0.27
CH$_3$COOH	CH$_3$COO$^-$	4.75	-0.28
pyridineH$^+$	pyridine	5.23	-0.31
ImH$^+$	Im	6.99	-0.41
hydrazineH$^+$	hydrazine	7.96	-0.47
Me$_2$ImH$^+$	Me$_2$Im	8.38	-0.50
NH$_4^+$	NH$_3$	9.23	-0.55
Me$_3$NH$^+$	Me$_3$N	9.80	-0.58
EtNH$_3^+$	EtNH$_2$	10.63	-0.63
Et$_3$NH$^+$	Et$_3$N	10.72	-0.63
Et$_2$NH$_2^+$	Et$_2$NH	10.80	-0.64
Bu$_2$NH$_2^+$	Bu$_2$NH	11.25	-0.67
H$_2$O	OH$^-$	14	-0.83

(Left margin labels: 0.71eV; Neutral Electrolytes)

Figure 4. The proton free energy level diagram for ionic liquids formed from moderately strong acid and moderately strong bases to yield neutral ionic liquid products. Arrows indicate the gap across which the proton falls in forming ethylammonium nitrate by the proton falling ouot of the occupied level on the HNO3 molecule into the vacant level on the ethylamine molecule

Likewise there is the possibility of a very strong base like the imine anion, NH^{2-} ion (for instance as sodium imine Na$_2$NH - analog of Na$_2$O) accepting a proton from a molecule that is normally a base. E.g. by analogy with water acting as an acid in its reaction with sodium oxide, ethylamine could become ethylamide, by the process

$$Na_2NH \ + \ CH_3CH_2NH_2 \quad \rightarrow \quad 2Na+ + NH_2^- \ + CH_3CH_2NH^-$$

NH$_2^-$ can be seen as the first member of (progenitor of) a large group of little- discussed salts anions that form a series of decreasing basicity, ranging from extreme base to the conjugate base of the superacid.. The series includes the following.

NH$_2^-$, CH$_3$NH$^-$, [CH$_3$NCH$_3$]-, through dicyanamide N(CN)$_2^-$ up to [CF$_3$SO$_2$NSO$_2$CF$_3$]$^-$

which latter is of course a very weak base, conjugate to the superacid HTFSI. The conjugate acids of these species can protonate any given base in an energy level below that of the acid, to generate a family of PILs.

Various physical properties of the PILs, (conductivities and viscosities, and by combination of these in the Walden plot, their ionicities, have been obtained, and are discussed in the attached JPC paper. To our disappointment we have found no cases in which there was a high degree of decoupling of proton motion from the motion of its vehicle base. A small "dry" proton contribution was identified, at lower temperatures, in the case of salts of the protic anions HSO$_4^-$ and H$_2$PO$_4^-$.

Enhancement of "dry" proton conductance fraction.

The "dry" (i.e. proton hopping motion) component can apparently be emphasized and made dominant by the repression of vehicular mobility via the crystallization of some acid salts. For instance, on crystallization, ethylammonium hydrogen sulfate, shows an increase in diffusivity of the proton whose resonance corresponds to the HSO_4^- proton, according to proton pulsed field gradient measurements which will be reported in setion B4 below.

2. *Fuel cell studies.*

Following the initial observations of Figure 2, we made Teflon sandwich cell measurements using ETEK electrodes using a wide variety of protic ionic liquids of differing proton transfer gap, and observed that the open circuit voltages of the cells generally correlated with the gap energy reaching the theoretical value when the gap was about 0.7-1.0 volts based on the ΔpK_a value. $\varepsilon = -(RT/F)\Delta pK_a$. This correlation, which was difficult to test in some cases because of extreme electrode wetting by the liquid, particularly in the case of fluorinated salts, has been shown in a recent publication in Chemical Communications in which we reported the surprising (because it was apparently not known before) observation that excellent fuel cell performance could be obtained using, as electrolyte, simple low melting mixtures of ammonium salts. These key results are shown in Figs. 5 and 6. The way in which the electrowetting problem for
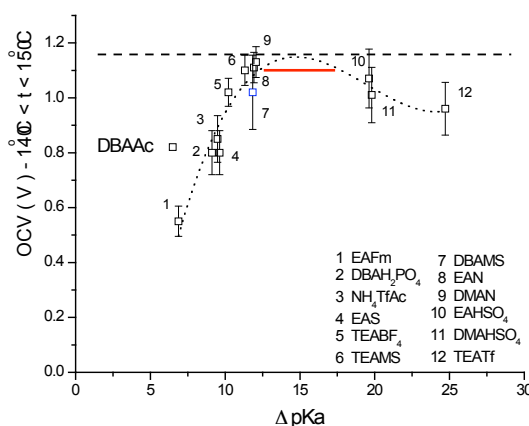
Figure 5. Open circuit cell voltages in relation to the proton transfer energy gap characterizing the protic ionic liquid electrolyte, showing the range of electrolytes that can yield theoretical fuel cell voltage.
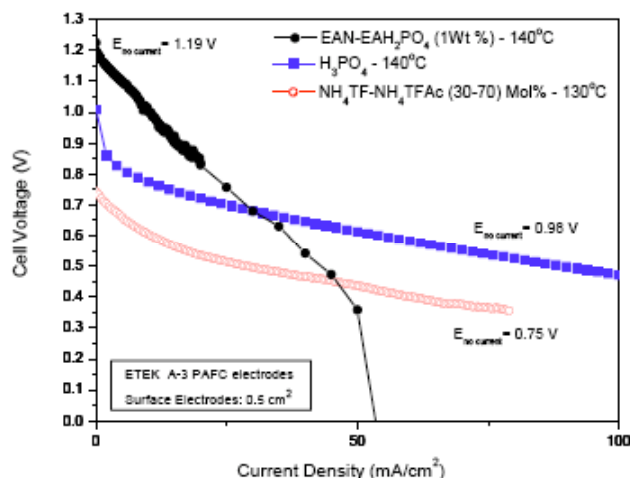
Figure 6. Total polarization curves for fuel cell with NH_4Tf-NH_4TFAc electrolyte, in comparison with those for phosphoric acid and dihydrogenphosphate-doped ethylammonium nitrate [xx], all measured in the same cell. The curves have been IR corrected. Anode and cathode are ETEK platinum catalyzed porous gas fed electrodes with Pt-loading = 0.5 mg/cm^2. Anode feed: hydrogen. Cathode feed: oxygen.

the organic cation electrolytes seems to be overcome in the case of the inorganic salt electrolytes is the key observation of Figure 6. Additional data for such systems are

8

shown in Fig 7 and the Tafel plot renditions of the data are shown in Figure 8. The vanishing slopes of the low current data in Figure 7 prove the absence of any energy barrier to oxygen reduction in these cases. The challenge now is to understand what it is that suddenly terminates this ideal behavior and causes the drop to the second current plateau. This urgent need will be vigorously pursued in our extended work on this project.

It is interesting to note that most aqueous electrolytes, like phosphoric acid and Nafion hydrated with excess water (> 3 water per SO3H group) have low open circuit potentials (< 1V vs RHE) whereas electrolytes based on PIL concept have open circuit voltages near or even exceeding the theoretical limit. The oxygen reduction electrode does not experience its thermodynamic potential of 1.2 V vs RH in aqueous electrolytes because metallic Pt, the oxygen electroreduction catalyst, does not begin form from the stable Pt-oxide at no lower potential than 0.95 V vs RHE, as shown by careful inspection of the voltammograms. Since the cell voltage is the difference of the hydrogen electrode and the oxygen electrode and the hydrogen electrode potential (0 V vs RHE), this oxygen electrode potential correlates well with the typical open circuit voltage of 0.95V for Pt-catalyzed fuel cells using the best aqueous electrolytes, such as Nafion. Since the PILs are non-aqueous electrolytes, it is not surprising that open circuit potentials can approach the theoretical limit, because there is no water to support Pt-oxide formation.

3. Membranes with good mechanical properties.

In the third component of the present project, we have studied, and to an extent mastered, the problems of providing polymer membranes with good mechanical properties to serve as the in-cell supporting structures for the ionic liquids of the above studies.

Pendant base vs pendant acid polymers, dry and IL-imbibed

The strategies followed in our membrane synthesis work have been based on attaching either proton-accepting, or proton-donating, groups to the most flexible polymer chain that we could provide. Thus we have synthesized siloxane chain polymers, critically cross-linked for mechanical strength, to which propylamine pendants are attached at every Si, in one case, and propylsulfonic acid groups are attached in the alternative case. Then the ionic polymer is created by:

        (a)   neutralizing the pendant amines either completely or partially with an acid such as methanesulfonic acid, or

        (b)   neutralizing the pendant acid groups either completely or partially with an amine such as methylamine.

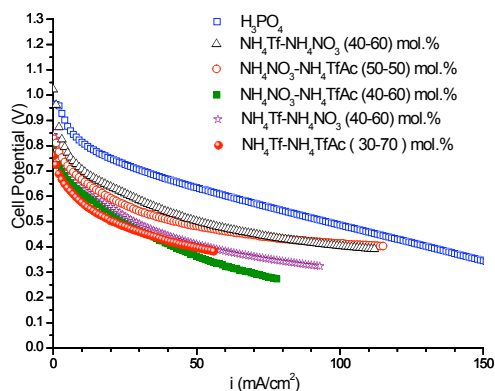   (c)   To increase the conductivity we then swell the respective polymers

Figure 7. IR-corrected polarization curves for cells using (1) ethylammonium nitrate, (2) ethylammonium nitrate doped with 1% ethylammonium dihydrogen phosphate,
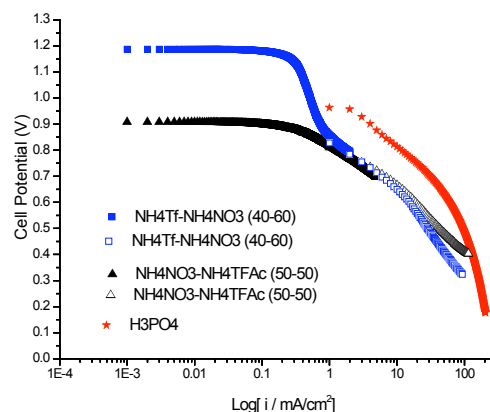
Figure 8. Polarisation curves for the two inorganic binary salts containing the nitrate anion, of Figure 7, shown in the Tafel plot form, cell voltage vs log current density. Overlap of data from independent runs using different current range instruments, establishes reproducibility of behavior. Plateau implies ideal (barrier-free) reduction at low current.

with a protic ionic liquid (ideally, this would not be necessary, but high conductivity seems to demand some sort of plasticizing agent)

Before ionic liquid plasticization, the above permits us to compare the fuel cell performance when the charge is carried across the polymer by the protonated amine (in case (b)) or by a Grotthus type exchange from cation-to-anion-to-neighboring-amine group (in case (a)). These two cases are referred to by us as "dry" polymer conductivity, It cannot be expected to be as high as when the membrane is swollen (plasticized) with ionic liquid of one type or another. The ion-swollen polymers reach conductivities as high as 10^{-2} S/cm at 100ºC (their minimum intended use temperature).

The data for conductivity of "dry" polymers are shown in Figures 9 and 10. The conductivities are seen to depend strongly on the extent of neutralization with the stoichiometric cases being the poorest conductors. The reason is clearly the excessive coulomb energy of the fully ionic polymer. The highest conductivity is obtained when every 8th pendant group is protonated. The data for the (PIL)-plasticized polymers are shown in Figs. 11 and 12. Not surprisingly, the conductivity maximizes at the highest ionic liquid content, structures. When only one in 8 of the pendant groups is neutralized, the conductivity passes through a maximum, The cohesion is indicated by the glass transition temperatures of the polymers which have also been measured, and which are shown in Figure11.

Our success with this scientifically challenging comparison has been very recent, the synthesis of the pendant sulfonic acid siloxane polymer having previously been a major

problem. The successful preparation, in partially neutralized form, is structurally illustrated in the following: .
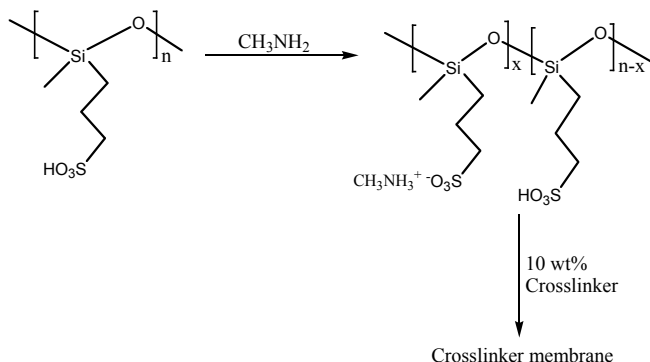
This neutralized conducting polymer can then imbibe ionic liquids of choice up to 60 wt %, yielding conductivities that are very high, exceeding 10 mScm^{-1} as illustrated in Fig. 12 below. Comparisons of this performance with published data are shown below in Figure 15
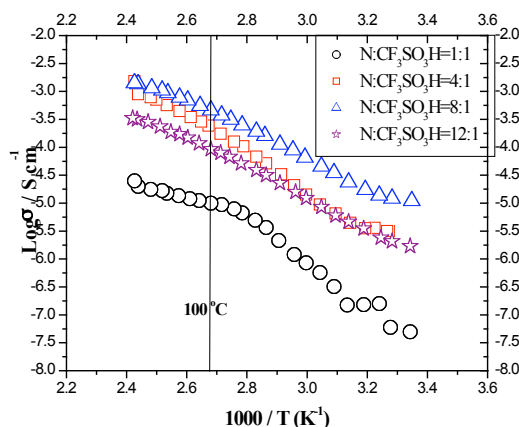

Figure 9. Conductivities of "dry" ionic siloxane polymers based on the neutralization of pendant propylamine groups to varying extents. Maximum conductivity of 10$^{-3.2}$ Scm^{-1} is reached when 1 in every 8 amines (12.5%) is neutralized. Conductivity decreases on crosslinking
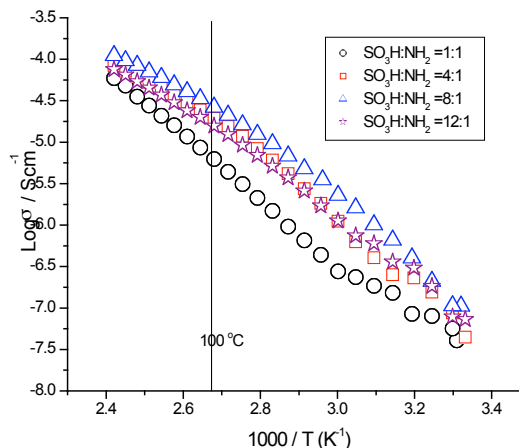
Figure 10. Conductivities of crosslinked "dry" ionic siloxane polymers based on the neutralization of pendant propyl sulfonic acid groups with methylamine, to varying extents. Maximum conductivity of **10$^{-4.5}$ Scm^{-1}** is reached when 1 in every 8 sulfonic acid groups is neutralized.
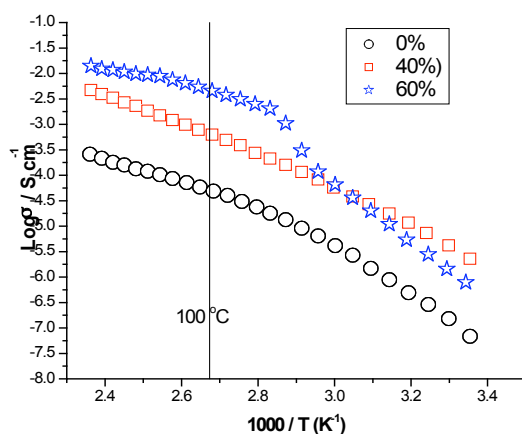
Figure 11. Conductivity of crosslinked siloxane polymers with pendant propylamine groups neutralized with methanesulfonic acid and then swollen with NH_4NO_3-$NH_4CF_3SO_3$ eutectic mixture. Conductivity at 60 wt% swell and 100°C is almost 10^{-2} Scm^{-1}.
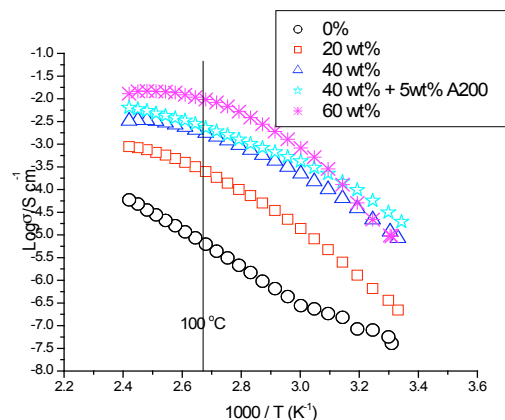

Figure 12. Conductivity of crosslinked siloxane polymer with pendant (propane) sulfonic acid, neutralized with methylamine and then swollen with NH_4NO_3-$NH_4CF_3SO_3$ eutectic mixture. Conductivity at 60 wt% swell and 100°C exceeds 10^{-2} Scm^{-1}.

Superior pendant base polymers

While we were working on a solution of the pendant acid siloxane problem, we synthesized a variant of the pendant base siloxane which has superior mechanical properties, due to facile crosslinking made possible by an intermediate NH group that is included in the pendant amine (which, accordingly, is now longer than before). The mechanical properties are comparable with those finally obtained with cross-linked siloxane chains with the pendant sulfonic acid groups, presumably due to additional between-chain hydrogen bonds. The new pendant base polymers can imbibe 60 wt% of ionic liquid without loss of mechanical viability.

The starting material for this approach is N-(2-aminoethyl)-3-aminopropyl-methyldimethoxy silane, $CH_3(CH_3O)_2Si$-$CH_2CH_2CH_2NHCH_2CH_2NH_2$. The idea is that the additional imine group in the middle of the pendant chain not only can provide additional reacting sites for acid doping and/or proton hopping, but also can provide additional membrane strength in terms of more interacting sites. Some results on conductivity in relation to temperature at different degrees of neutralization, and also different ionic liquid loadings, are given in Figs. 13 and 14, respectively.

The conductivity is very sensitive to the type of acid used and to the ratio of acid to pendant base. Highest conductivity was obtained when only 25% of the pendant groups were neutralized (with methane sulfonic acid). With ionic liquid swelling, increases up to 10 mScm^{-1} at 100°C can be obtained without loss of mechanical strength. This is a very promising ion-conducting polymer.

A membrane made from this polymer, swollen with NH_4NO_3-NH_4Tf eutectic, was used in the trial fabrication of a gas diffusion fuel cell. The cell yielded a very pleasing 1.15 V open circuit potential, but unfortunately failed under load before it could be

properly evaluated, partly due to mechanical problems.We plan to carry out more extensive fuel cell tests of these newer, mechanically sound, membranes in the coming year if this extension proposal is funded.

Comparisons with previous work

These results compare favorably with the best in the literature. For instance Yamada and Honma(*22*) have prepared a polyphosphinic acid polymer with pendant H_2PO_4 groups which, when heavily plasticized with the base imidazole, exhibits a conductivity of $10^{-2.2}$ S cm^{-1}. Without plasticization (i.e. when dry) the conductivity is very low. Honma and Yamada have described other imaginative systems which they argue are "dry" proton conductors, one based on a phosphotungstic acid-polystyrene sulfonic acid complex(*23*) and another based on methanediphosphinic acid chitosan polymer which reach conductivities close to 10^{-2} S/cm at 100ºC, and a mesoporous ceramic-based system that apparently reaches a conductivity of 2 x 10^{-2} S/cm.

Kreuer's group is perhaps the most experienced in proton transport. His group has worked with polymeric systems with tethered bases for many years, but their "dry" polymers never exhibit conductivities above about 10^{-5} S/cm. They have provided an excellent review, reporting on achievements up to 2004(*24*).

Finally, there is the protic IL-plasticized polymer of the Kinder group, which has been our approach, was mentioned in the introduction. We reproduce, below, in Fig. 15, a **conductivity vs temperature** plot from their study, onto which the results of our own work, and of the imidazole-plasticized phosphinic acid of Honma and Yamada have been placed for comparison. All are comparable though own present data are a little higher.
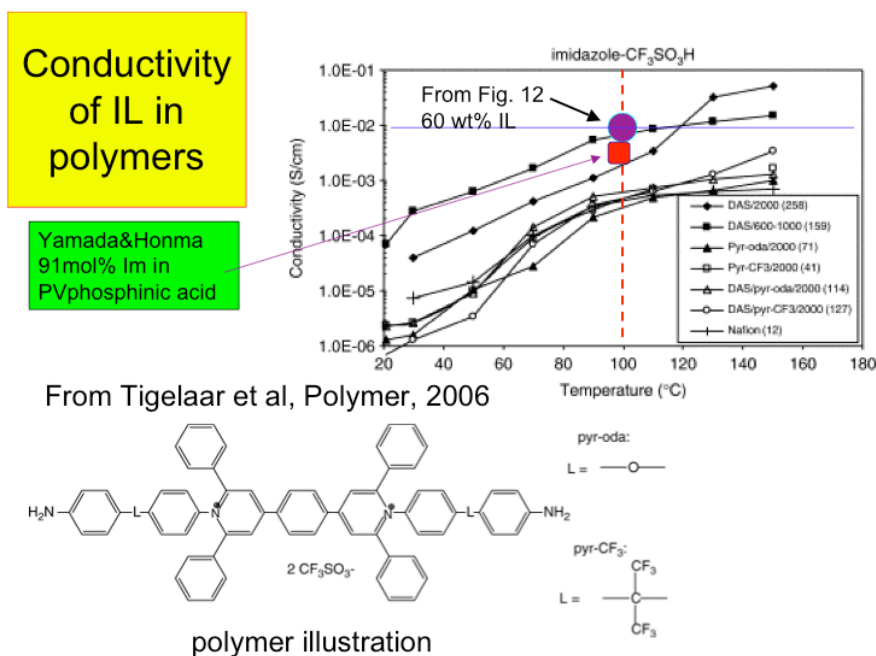.

Figure 15. Results of protonic liquid-swollen, rod-like, polymers from the work of Tigelaar et al(*19*) with best results from the work of Honma and Yamada(*25*), and from the present work, superimposed for comparison.

Before proposing a program of further research to take advantage of the advances that we have reported above, we must mention additional results that we have achieved in the area of crystalline rotator phase conductivities

4. Solid ionic conductors with high "dry" proton conductivity.

In our original proposal we identified certain plastic crystal systems that had remarkably high ionic conductivities. We proposed to study these and related systems, but for practical interest we needed to have much higher temperature ranges available. In the past year we researched and reported work on various mixed organic cation-inorganic cation mixtures some of which had very high conductivity at 100°C. We have a manuscript (now published in J. Non-Crystalline Solids(*26*) –see publications from the grant at end of project description) which contains some data on systems related to the celebrated $CsHSO_4$ "dry" proton conductor. Our contribution was to incorporate an organic cation in the rotator phase to stabilize it to lower temperatures. Data in the final figures of this MS) suggest the existence of a mixed cation solid state conductor with conductivity of about 10^{-2} S/cm.

In current work we have performed pulsed field gradient spin echo diffusion measurements and find that there are protons associated with HSO_4^- and $-NH_3^+$ sites with diffusion coefficients of liquid-like values, consistent with the high conductivity, however the protons on the same species carrying the $-NH_3^+$ group has an immeasurably low diffusion coefficient except perhaps at the highest temperatures. This is strong evidence that the protons on the ammonium moiety and the HSO_4^- species are highly decoupled from their hosts. The high conductivity extends down to temperatures approaching room temperature where a phase change occurs.

A first attempt to incorporate a film of this material as electrolyte in a fuel cell was successful but there were mechanical issues which might be resolved in further tests in the extension period if this proposal is granted.

5. Glass electrodes for fuel cell effective pH studies

In our development of the subject of protic ionic liquids we have proposed the use of Gurney type proton free energy level diagrams to organize the thinking and the data on proton transfer processes involved in the consideration of the nature of protic ionic liquids. There is no equivalent of this in the field of aprotic ionic liquids that are formed by irreversible synthetic steps which are undone on heating only by decomposition. Recognizing the weakness of using pK_a data obtained from aqueous solution studies in the assignment of energy levels(*21*), we have begun consideration of the means of obtaining energy level data appropriate for the unhydrous systems. We have also recognized the utility of the N-H proton chemical shift to give us a direct guidance on the state of the proton after transfer from the acid to the base.

We have correlated the proton chemical shift with an electrochemical measure(*27*) obtained by modifying a conventional glass electrode to have an ionic liquid rather than an aqueous phase in contact with the reference calomel electrode. However this is only a temporary step. While the voltage read out (effective pH) that we obtain correlates linearly with the N-H chemical shift the calibration adjustment is very large reflecting the large free energy difference between protons in aqueous solution and protons in the ionic liquid, and the precision will therefore not be high.

We have redesigned the entire electrode to reflect the ionic liquid environment. We expect that this new (and patent-protected) device(*28*) will find broad application in the ionic liquid research field.

PUBLICATIONS AND PRESENTATIONS FROM THE GRANT.

1. Highly decoupled ionic and protonic solid electrolyte systems, in relation to other relaxing systems and their energy landscapes". F. Mizuno*[#], J.-P Belieres*, N. Kuwata[@$], A. Pradel[@], M. Ribes[@], and C. A. Angell*, J. Non-Cryst. Sol., (online at http://dx.doi.org/10.1016/j.jnoncrysol.2006.06.006)

2. Binary Inorganic salt mixtures as high conductivity electrolytes for >100ºC fuel cells J.-P. Belieres, D. Gervasio, and C. A. Angell, Chem. Commun. 2006, **DOI:** 10.1039/b611150e

3.   Protic ionic liquids: Preparation, characterization , and the proton transfer energy level diagram.. (invited for special issue on Ionic Liquids. J.-P. Beleieres and C. A. Angell, *J. Phys. Chem. B,* **111** (18), 4926 -4937 (2007

4.   Parallel developments in inorganic, aprotic, and protic ionic liquids: physical chemistry and applications" C. Austen Angell, Nolene Byrne and Jean-Philippe Belieres, Accounts of Chemical Research (special issue on Ionic Liquids) **40**, 1228-1236, (2007)

     In preparation.
1. Crosslinked siloxane polymers with pendant cations, "dry" and IL-plasticisized, for fuel cell membranes, Xiaoguang Sun, Don Gervasio and C. Austen Angell,

2. Crosslinked siloxane polymers with pendant anions, "dry" and IL-plasticisized, for fuel cell membranes, Xiaoguang Sun Don Gervasio and C. Austen Angell

3. Proton diffusivity and conductivity in solid organic cation salts. Nolene Byrne, Don Gervasio and C. Austen Angell.

4   Proton transfer energies , Diffusivities, Nernst-Einstein conductivity ratios and ionicity in protic ionic liquids of different proton energy gaps. Nolene Byrne, Jean-Phillippe Belieres, Don Gervasio and C. Austen Angell

PRESENTATIONS BASED ON WORK PERFORMED UNDER THIS GRANT

PRESENTATIONS BASED ON WORK PERFORMED UNDER THIS GRANT

A. **by C. Austen. Angell**

1. Opening talk at COIL II (2nd. International conference on Ionic Liquids.
   C. A. Angell, N. Byrne, J-P. Belieres, **"Proton activity in ionic liquids: The ILPA index and its application in optimizing fuel cell efficiency, protein stability, and large molecule solubility".** Yokohama, Japan, August 5th, 2007

2. Plenary talk at 16th Solid State Ionics conference (SSI-16) Shanghai, China, July 1-6 (2007) C. A. Angell**. "On the relation of "dry" proton to "fast" Li+ conductivity in crystalline, glassy and polymer solid electrolytes,"**

B. **by Don. Gervasio**

1. Invited Talk **"Protic Salt Polymer Membranes: Water-Free Proton-Conducting Membranes",** Southeast Regional Meeting American Chemical Society (SERMACS), Greenville, SC, October 26, 2007.

2. Invited talk **"Fuel Cells for Clean Power and Energy"**, Korean Electrochemical Society, Seoul Korea, Friday October 5, 2007.

3. Invited Talk **"Protic Salt Polymer Membranes: High-Temperature Water-Free Proton-Conducting Membranes"**, FreedomCar Fuel Cell Tech Team (GM, Ford, Chrysler, DoE), Detroit, MI June 20, 2007.

4. Invited Talk **"High temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFCs) for Portable Power in Large-Scale Energy Storage Devices",** Paper Number 195, 212th Meeting of the Electrochemical Society, Washington DC, October 11, 2007.

5. Invited Talk **"Proton transfer salts: A new class of solvent-free, involatile, fuel cell electrolytes",** D. F. Gervasio, J-P Belieres, and C. Austen Angell, paper number 171, presented to American Chemical Society, Division of Fuel Chemistry, Fuel Cell Chemistry and Operation, San Francisco, CA, September (2006).

6. Invited Talk **"Proton Transfer Salts: a New Class of Solvent-free, Involatile, Fuel Cell Electrolytes",** Don Gervasio (speaker), Jean-Philippe Belieres, C. Austen Angell, H. Markusson (Chalmers University of Technology), and W. Xu (Ferro Corporation), Electrochemical Society, 2nd International Conference on Polymer Batteries and Fuel Cells, Riviera Hotel, Las Vegas, Nevada, USA Ex. Abstract No. 205 (2005).

C. **by Jean-Philippe Belieres**

1. Jean-Philippe Belieres, Xiao-Guang Sun, Don Gervasio and C. Austen Angell, **Ionic liquids and fuel cell membranes: a new generation of polymer electrolyte fuel cell membranes using the anhydrous protic ionic liquid principle**, *PIRA conference on Ionic Liquids, Orlando, FL,* December 11-13, 2006

2. J.-P. Belieres, N. Byrne, X. Sun, D. Gervasio, J. Yarger and C. A. Angell, **Binary inorganic salt mixtures as high conductivity liquid electrolytes for high temperature fuel cells,** *Division B2 - Advanced Materials for Fuel Cells and Batteries - Abstract #321, The Electrochemical Society, Chicago, IL,* May 6-10, 2007

3. J.-P. Belieres, N. Byrne, D. Gervasio, C. A. Angell, **Protic ionic liquids and the PEM fuel cell,** *2nd International Congress on Ionic Liquids, poster session, #3P07-081, Yokohama, Japan,* August 5-10, 2007

D. **by Xiao-Guang Sun**

1. **Xiao-Guang Sun, Jean-Philippe Belieres, Don Gervasio, C. Austen Angell, Development of materials having high ionic conductivities for high temperature fuel cell applications**, The 208th Meeting of The Electrochemical Society, Los Angeles, CA, Oct. 16-21, 2005, Abs. #928.

2. Xiao-Guang Sun, Don Gervasio, C. Austen Angell, **High temperature fuel cells using ionic polysiloxane membranes, with and without ionic plasticizers**, The 213th Meeting of The Electrochemical Society, Phoenix, AZ, May. 18-22, 2008, Abs. #442.

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Protic Ionic Liquids: Preparation, Characterization, and Proton Free Energy Level Representation[†]

Jean-Philippe Belieres and C. Austen Angell*

Department of Chemistry and Biochemistry, Arizona State University, Tempe Arizona 85287-1604

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We give a perspective on the relations between inorganic and organic cation ionic liquids (ILs), including members with melting points that overlap around the borderline 100 °C. We then present data on the synthesis and properties (melting, boiling, glass temperatures, etc.) of a large number of an intermediate group of liquids that cover the ground between equimolar molecular mixtures and ILs, depending on the energetics of transfer of a proton from one member of the pair to the other. These proton-transfer ILs have interesting properties, including the ability to serve as electrolytes in solvent-free fuel cell systems. We provide a basis for assessing their relation to aprotic ILs by means of a Gurney-type proton-transfer free energy level diagram, with approximate values of the energy levels based on free energy of formation and pK_a data. The energy level scheme allows us to verify the relation between solvent-free acidic and basic electrolytes, and the familiar aqueous variety, and to identify neutral protic electrolytes that are unavailable in the case of aqueous systems.

Introduction

Ionic liquids (ILs), and particularly room-temperature ILs, have attracted much attention in recent years, and many new applications beyond green chemistry continue to be found. They are the low-melting relatives of molten salts whose place in the history of chemical innovation goes back to the foundations of chemistry. Many of the elements of our periodic table were first revealed by the electrolysis of one or other "ionic liquid" in the form of molten halides.[1] The difference is only that, by use of large compound cations to reduce the coulomb attractions to anions and complicated shapes to confuse the ion packing problem, the crystalline state of the system is sufficiently destabilized for melting to occur near to or below ambient.[2]

Because of the differences in properties between the average IL and the average high-temperature molten salt (e.g., 2 orders of magnitude in conductivity and fluidity, non-Arrhenius vs Arrhenius temperature dependences of these properties, etc.), and because of the differences in their applications in industrial chemistry (e.g., winning of aluminum vs solvent function for synthetic inorganic chemistry) there has developed some sort of schism between the different branches of the IL field. We commence this article with a reminder of the essential artificiality of this division and then draw attention to a further division in the field, which is of a qualitatively different type.

In Figure 1a, we make an Arrhenius plot comparison of the viscosities of various members of the inorganic and organic cation family of molten salts, and then in Figure 1b show the same data in scaled Arrhenius plot form using the calorimetric glass temperature, T_g, to scale the temperature. T_g serves as a cohesive energy parameter,[2] and Figure 1b shows that when scaled for cohesive energy it is no longer possible to tell the difference between the salts with inorganic cations and those with molecular (organic) cations. The same type of scaling (using *ideal* glass temperatures) was used long ago to relate molten salt hydrates to anhydrous molten salts.[3]
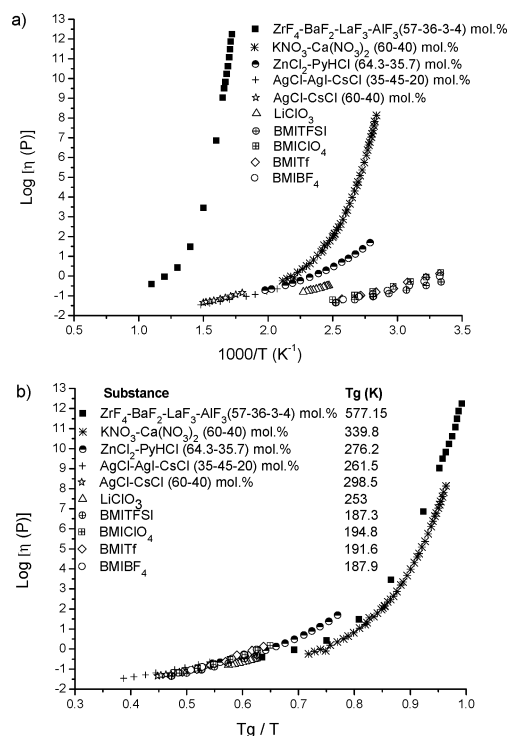

Figure 1. (a) Arrhenius plot of viscosity data on molten salts and on ILs. (b) T_g-scaled Arrhenius plot of the same data, showing underlying similarity.

While applications of molecular cation ILs have been dominated by their solvent function,[4,5] there are now developing new applications in which the electrical charges on the ions are specifically employed. A good example is that of electrolytes for photoelectrochemical (solar) cells.[6] Recently a new and potentially important application of ILs has been recognized— that of the electrolyte in a fuel cell.[2,7,8] This is an application which requires the presence of a special type of ionic liquid— one in which the cation provides a vehicle for exchangeable protons. We refer here to the ILs formed by proton transfer
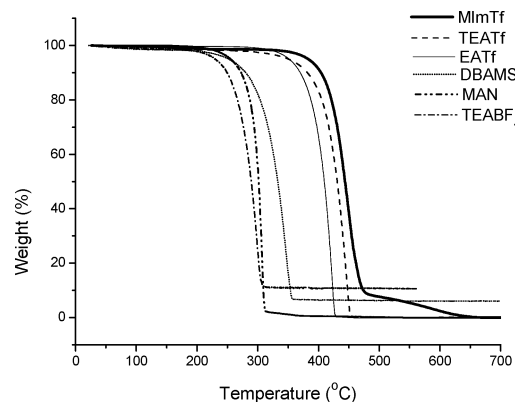
Figure 2. TG scans of a selection of PILs, showing their varying thermal stabilities.
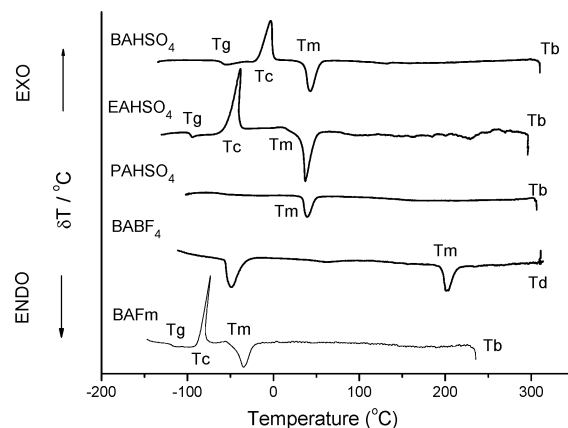

Figure 3. DTA scans for some PILs from this study. Arrows indicate successive thermal events, glass transition temperature T_g, crystallization temperature T_c, melting point T_m, and boiling point T_b (endothermic) or decomposition temperature Td (exothermic).

from a Brönsted acid to a Brönsted base, i.e., by the method used to make the first recorded ambient temperature ionic liquid nearly a century ago.[9] These are ILs of a qualitatively different type, because their ionicity is adjustable, by virtue of the different driving forces for the proton-transfer that can be chosen.

Protic ILs (PILs), such as pyridinium chloride,[10] have long been used as sources of highly basic chloride ions for spectroscopic studies[11] and also as a means of obtaining low-melting salt mixtures,[12] but such studies have been made mainly by physical chemists interested in accessing the "low-temperature domain" of liquid behavior. Since "ILs" became attractive as synthetic media, many protic ILs have been reported, particularly by Ohno and co-workers.[13–15] To provide ILs that were unequivocally ionic, Ohno and co-workers used proton transfer from a very powerful acid, hydrogen bis-trimethylsulfonyl imide, HTFSI, the conjugate base of which is an anion that is well known for promoting low melting points. In a more recent study, our own group has explored the relationship between this proton-transfer process and the nature of the acid transferring the proton.[16,17] We have demonstrated[16] that the melting points and glass transition temperatures tend to be lower, and the conductivities tend to be higher, for the protic than for the aprotic ILs, even though the conductivity at a given viscosity tends to be the same (Walden rule).

Applications of nonaqueous protonated Brönsted bases in fuel cell technology have been focused on the imidazole molecule, the use of which as a carrier of protons in a fuel cell was introduced in 1998.[18] In the latter studies the carrier was incorporated with polymeric anions as a membrane. More recently,[7,19] neat protic ILs were shown to serve well in place of acid or base electrolytes in simple bubbler cells. The most surprising finding[2,20,21] is that the polarization of the oxygen electrode, always a major problem for the efficiency of fuel cells, can be almost overcome in an ionic liquid fuel cell with high area catalyst surface cathodes when the right protic IL is used. The slope of the Tafel plot (cell voltage vs log current) that is proportional to the energy barrier opposing the electron-transfer process proves to be almost zero.

This latter finding has stimulated a major synthetic and testing effort in our group, involving the preparation of protic salts utilizing a wide variety of acid + base combinations in the effort to find systematic trends in the properties of the resulting salts and particularly in the open-circuit voltages of H_2/O_2 fuel cells utilizing the salts as electrolytes. The results of the latter study will be reported elsewhere.[21] Here we present and discuss the findings for the basic physical and electrochemical properties of the protic salts, some 103 in total number.

Experimental Section

Materials. Anhydrous trifluoromethanesulfonic acid (triflic acid, HTf, 99%) was obtained from Alfa Aesar. Anhydrous difluorophosphoric acid was obtained from SynQuest Labs Inc. Anhydrous formic acid (HFm, 98%) was obtained from Fluka. Analytical reagents phosphoric acid (85%, ACS grade) and sulfuric acid (95–98%, ACS grade) were obtained from Mallinckrodt Chemicals. Nitric acid (68–70%, GR ACS grade) was obtained from EMD Chemicals Inc. The acids methanesulfonic acid (70 wt.% in water), tetrafluoroboric acid (48 wt.% in water), and hydrofluoric acid (HF, 48%) and the bases methylamine (MA, 40 wt.% in water), ethylamine (EA, 70 wt.% in water), propylamine (PA, 99+%), butylamine (BA, 99.5%), tert-butylamine (tBA, 99.5+%), 2-methoxyethylamine (MOEA, 98%), 3-methoxypropylamine (MOPA, 99%), dimethylamine (DMA, 40 wt.% in water), diethylamine (DEA, 99+%), dibutylamine (DBA, 99.5+%), *N*-methylbutylamine (MBA, 96%), *N*-ethylbutylamine (EBA, 99%), trimethylamine (TMA, 99.5%), triethylamine (TEA, 99.5%), tributylamine (TBA, 99%), *N,N*-dimethylethylamine (DMEA, 99%), aniline (An, ACS reagent >99.5%), 2-fluoropyridine (FPy, 98%), imidazole (Im, 99+%), 1-methylimidazole (MIm, 99+%), and 1,2-dimethylimidazole (DMIm, 98%) were obtained from Aldrich Chemical Co. All chemicals were used as received.

PILs are formed by proton transfer between a Brönsted acid and a Brönsted base. An equimolar amount of acid and base, either neat or in an aqueous solution, are reacted together. Since these reactions are very exothermic, the dropwise addition of the acid to the amine was carried out by cooling the amine solution to −78 °C, using an acetone/dry ice bath. The mixture was then stirred at room temperature for several hours. To ensure a complete reaction, a slight excess of amine was used and then removed along with the water by heating at 80 °C in vacuum using a rotary evaporator. The same general process may be used for the synthesis of all PILs, but when amines of higher molecular weight are employed, there is a risk of contamination of the product by residual amines. When necessary, adequate purification procedures were applied.[4,22] The product was then dried at 80 °C for 2 days in a vacuum oven containing phosphorus pentoxide P_2O_5 to remove any excess water. For most of our syntheses, the reactions were carried out without any solvent at all. The structure of each PIL was identified by NMR spectroscopy and/or by elemental analysis. The complete removal of water and the absence of other −OH-containing species were confirmed by the absence of O−H stretching bands from

TABLE 1: Glass Transition Temperatures for Selected PILs of This Study[a]

cation	HCOOH ($R = 1.69$)	H$_2$F$_2$ ($R = 1.72$)	HNO$_3$ ($R = 1.79$)	H$_2$SO$_4$ ($R = 1.90$)	H$_3$PO$_4$ ($R = 2.00$)	CH$_3$SO$_3$H ($R = 2.24$)[b]	HBF$_4$ ($R = 2.30$)	CF$_3$SO$_3$H ($R = 2.70$)
NH$_4$		n.d.[b]	n.d.	−65.6	−23.3			
MA	−108.2	−104.1	n.d.	n.d.	−28.8	n.d.	n.d.	
EA	−127.5	−100.3	−91.5[c]	−96.4	−31.3	n.d.	n.d.	n.d.
BA	−120.1			−63.4	−33.3	−89.6	n.d.	
DMA	n.d.	−111		n.d.	−36.8	−95		
DBA	−116.4			n.d.	−15.6	−49	n.d.	
TEA				−100.1	−34.4	−96.5	n.d.	n.d.
DMEA	−121.1			−91.4		n.d.		
Im			n.d.[e]				n.d.	n.d.
Mim			n.d.[e]				n.d.	45.8
Eim			n.d.[e]				−87[e]	n.d.[e]
DMIm			n.d.[e]				−74.7	n.d.[e]
EMIm			n.d.[e]				−88	

[a] Anion radius in angstroms. [b] Reference 36. [c] Not detected. [d] Extrapolated from ref 38. [e] Reference 37.

3400 to 3800 cm^{-1} in the infrared spectra of the final melts. The PILs were then stored in an argon atmosphere glovebox (VAC, O$_2$ < 1 ppm and H$_2$O < 1 ppm).[23] In the case of EAN, a Karl Fisher water titration device was used to determine that the water content was less than 0.025 wt.%.

The thermal transitions of interest to this work were determined using a simple home-made DTA instrument[24] comprising a twin thermocouple setup employing twin digital voltmeters with microvolt sensitivity, interfaced to a laboratory computer for readout and recording purposes. One reason for choosing the DTA technique over the better-controlled differential scanning calorimetry technique is that, with DTA, samples can be taken to their boiling points without endangering the instrumentation. Boiling points, where the total pressure of all species in the vapor-phase reaches 1 atm, provide a useful metric of the energy of the proton-transfer process and of course fix the temperature range of application of the ionic liquid in question. The boiling points are signaled by a sharp endothermic effect as the enthalpy of vaporization (involving relocation of proton on the acid) is absorbed.

The DTA sample holder assembly consists of an aluminum temperature-smoothing block with two wells to contain Pyrex glass sample and reference tubes (3 mm outside diameter) into which thermocouples could be inserted. The aluminum block holder was heated from −150 to +400 °C by two 200-W heating cartridges, symmetrically disposed. The heating rate was controlled by a Barnant Co. temperature controller, model 68900-11 interfaced to a computer. For reproducibility purposes, it is important to ensure that the thermocouple and container are consistently located at the same depth in the block. The two K-type thermocouples are connected in opposition so that the ∼μV voltage differences between the sample and the reference can be read out. The output of the reference thermocouple was used separately to determine the temperature at which any thermal event of interest occurred. Anhydrous alumina was used as reference material. About 0.2 mL of the solution was loaded into the DTA sample cell. The thermocouples, protected by fine glass capillary tubes, were immersed to 50% depth in the sample and reference material, respectively. A plug was made by wrapping Teflon tape around the capillary tube. Samples were quenched in liquid nitrogen, inspected for state of vitrification, and then scanned during warm-up at 10 K/min. After appropriate calibration with melting point standards, this simple instrument is able to define melting points with an accuracy and precision of ±1 °C.

Ionic Conductivities. Ionic conductivities were determined from complex impedance data from an automated HP 4192A

Impedance Analyzer with a frequency range of 5 Hz to 13 MHz. Heating or cooling rates were controlled by a Barnant Company Temperature Controller model 68900-11 at a standard rate of 1 °C/min. The dip-type conductivity cells for liquid electrolytes were constructed with platinum electrodes sealed in soft glass. Cell constants of about 1 cm^{-1} were determined using a standard 0.1 N KCl solution. Approximately 0.5 to 1 mL of solution was needed to perform an experiment. During measurement, the temperature of the sample was monitored using a K-type thermocouple. The conductivity was determined from the initial part of the almost frequency-independent plateau of the log-(conductance) vs log f plot. Values obtained were checked against the data obtained by short extrapolation to the real axis of the usual complex impedance plot.

Density Values. Density values with an accuracy of 0.5% were measured in a VAC drybox simply by measuring the weight of the sample filling a 2-mL volumetric flask at different temperatures. Before each measurement, the flask was maintained in a heating block at the desired temperature for half an hour until the temperature was steady.

Kinematic Viscosity Measurements. Kinematic Viscosity Measurements were performed using Cannon-Ubbehblde viscometers designed for transparent liquids between 0 and 150 °C. For measurements at a higher temperature, we used a specially designed aluminum block holder heated by two 200-W heating cartridges symmetrically disposed. The heating was controlled by the same Barnant Co. system referred to above. The temperature of the sample was maintained for half an hour before measurement. CaCl$_2$ drying tubes were used to protect the samples from moisture. The precision of measurement with Cannon-Ubbehblde viscometers is determined by the reproducibility of the flow time. Because we were using a single viscometer for each sample, the precision was limited at the highest temperatures by the short flow times (<10 s). The flow times were reproducible and the standard deviation was ±0.2 s. For temperatures below 40 °C, the run times are typically 200 s or longer, hence the reading error is only 0.1% of the efflux time.

Thermogravimetric Analysis (TGA). TGA experiments were performed using a TA Instruments high-resolution TGA 2950 thermogravimetric analyzer. The samples were weighed and placed in a platinum crucible. They were then heated from room temperature to 700 °C with a heating rate usually of 10 °C/min. The sample chamber had a controllable environment to allow monitoring of the degradation under various conditions (air, oxygen, or dry nitrogen).

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TABLE 2: Melting Point, T_m (°C) of Some PILs of This Study[a]

cation	HCOOH (R = 1.69)	H$_2$F$_2$ (R = 1.72)	HNO$_3$ (R = 1.79)	H$_2$SO$_4$ (R = 1.90)	H$_3$PO$_4$ (R = 2.00)	CH$_3$SO$_3$H (R = 2.24)[b]	HBF$_4$ (R = 2.30)	CF$_3$SO$_3$H (R = 2.70)
NH$_4$	120	125.6	163.5	116.3	193.3			225
MA	−21.7	−11.8	104.7	73.2	96.8	91	77.1	
EA	−72.9	3.5	13	31.9	109.5	112.5	152.4	172.1
BA	−46.8			33.5	113.3	131.8	198.2	
DMA	n.d.[c]	−22.9	75	40.1	117.3	122.1		
DBA	n.d.			130.9	98	42.7	212.8	
TEA				84.2	n.d.	21.6	104.3	n.d.
DMEA	n.d.			3.3		94.7		
Im							131.2	122.9
MIm			70[d]				35.8	92
EIm			31[d]				n.d.[d]	8[d]
DMIm			84[d]				31.3	119[d]
EMIm			75[d]				n.d.[d]	33[d]

[a] Anion radius in angstroms. [b] Reference 36. [c] Not detected. [d] Reference 37.

TABLE 3: Thermal Transition Temperatures for Formates

IL cation	symbol	T_g (°C)	T_c (°C)	T_m (°C)	T_b (°C)	ΔpK_a
ammonium	AFm			120		5.5
methylammonium	MAFm	−108.2	n.d.[a]	−21.7	162.1	6.9
ethylammonium	EAFm	−127.5	n.d.	−72.9	176.1	6.9
propylammonium	PAFm	−124.7	n.d.	−55.4	213.1	6.8
butylammonium	BAFm	−120.1	−89.8	−46.8	224.5	6.9
hydroxyethylammonium	HOEAFm	−88.3	n.d.	n.d.		9.1
methoxyethylammonium	MOEAFm	−103	n.d.	−22.4	209.1	5.7
methoxypropylammonium	MOPAFm	−116.4	n.d.	n.d.		6.0
dimethylammonium	DMAFm	n.d.	n.d.	n.d.	152	7.1
dibutylammonium	DBAFm	−116.4	n.d.	n.d.	234.7	7.5
dimethylethylammonium	DMEAFm	−121.1	n.d.	n.d.	187.4	6.2
ethylbutylammonium	EBAFm	−119.6	n.d.	n.d.	207.3	7.1
hydrazinium[b]		−87		44.3		4.2

[a] Not detected. [b] Reference 27.

TABLE 4: Thermal Transition Temperatures for Nitrates

IL cation	symbol	T_g (°C)	T_c (°C)	$T_{S_1 \rightarrow S_2}$ (°C)	T_m (°C)	T_b (°C)	ΔpK_a
ammonium	AN[a]	n.d.[b]	n.d.	46.7	163.5	223.8	10.5
methylammonium	MAN[a]	n.d.	n.d.	73.5	104.7	206.8	11.9
ethylammonium	EAN	−91.5[c]	−59.1	−43.8	13	240	11.9
hydroxyethylammonium	HOEAN	−87.4	−52.6	n.d.	−25.2	255.4	14.2
methoxypropylammonium	MOPAN	−82.7	n.d.	n.d.	n.d.		11.0
dimethylammonium	DMAN	n.d.	n.d.	22.4	75	explosive	12.1
methylbutylammonium	MBAN					explosive	12.2

[a] From differential scanning calorimetry data. [b] Not detected. [c] Extrapolated from ref 38.

TABLE 5: Thermal Transition Temperatures for Perchlorates

IL cation	symbol	T_g (°C)	T_c (°C)	T_m (°C)	T_b (°C)	ΔpK_a
ethylammonium	EAClO$_4$	n.d.[a]	n.d.	151.9		20.6

[a] Not detected.

Results

TGA. The thermogravimetric analysis curves of several protic ILs are shown in Figure 2. The thermal stability is seen to vary with the cation−anion combination under study, being highest when the cation is aromatic in character (methylimidazolium) and the anion a very weak base (triflate). The weight loss begins at the boiling point for low-energy proton transfers (methylammonium nitrate). For PILS formed with large proton-transfer energies (see Discussion section), boiling would only occur at very high temperatures and is pre-empted by chemical decomposition.

These TGA curves confirm the formation of protic neutral salts since we have one-step weight loss processes. In case of acid or base excess compositions, the TGA curve would show a two-step process, with the initial loss corresponding to the excess of acid or base in the system.[25]

Thermophysical Properties. Some representative DTA scans for protic ILs of this study are shown in Figure 3 to indicate the variety of signals that can be obtained for different cases and the manner in which the transition temperatures are defined from these signals.

In Tables 1−12, we record data for the various transition temperatures that can be observed: glass temperatures (if the liquids can vitrify), solid-state transition temperatures ($T_{S_1 \rightarrow S_2}$, ...), melting points, and "boiling points", respectively. Tables 1 and 2 show a single property (glass temperature T_g in Table 1, and melting point T_m in Table 2) for a variety of cations (descending), one column for each anion type, so that the trends in these two most important properties can be seen. Then, Tables 3−12 record the data on all transitions for all the cations studied, one table for each anion, the tables being ordered by increasing anion complexity, as follows:

Table 3, formates (2 oxygens);
Table 4, nitrates (3 oxygens);
Table 5, perchlorates (4 oxygens);
Table 6, tetrafluoroborates (4 fluorines);

TABLE 6: Thermal Transition Temperatures for Tetrafluoroborates

IL cation	symbol	T_g (°C)	T_c (°C)	$T_{S_1 \rightarrow S_2}$ (°C)	T_m (°C)	T_{dec} (°C)	ΔpK_a
ammonium	NH₄BF₄					dec	8.7
methylammonium	MA BF₄			−24.9	187.8		10.1
ethylammonium	EABF₄				152.4		10.1
butylammonium	BABF₄	n.d.ᵃ	n.d.	−55.9	198.2	310.5	10.1
tert-butylammonium	tBABF₄	n.d.	n.d.	−53.8	118.3	243.6	10.2
hydroxyethylammonium	HOEABF₄				0.5		12.4
methoxyethylammonium	MOEABF₄				n.d.	206.9	9.0
dibutylammonium	DBABF₄	n.d.	n.d.	−13	212.8	330.1	10.8
methylbutylammonium	MBABF₄	n.d.	n.d.	−83.9	77.1	350.3	10.4
triethylammonium	TEABF₄	n.d.	n.d.	−56.8	104.3	286.7	10.2
imidazolium	ImBF₄	n.d.	n.d.	−86.3	131.2	363.2	6.5
1-methylimidazolium	MImBF₄	n.d.	n.d.	−25.7	35.8	387	6.6
1,2-dimethylimidazolium	DMImBF₄	−74.7	−1.3	n.d.	31.3	365.2	7.9

ᵃ Not detected.

TABLE 7: Thermal Transition Temperatures for Triflates

IL cation	symbol	T_g (°C)	T_c (°C)	$T_{S_1 \rightarrow S_2}$ (°C)	T_m (°C)	T_b (°C)	ΔpK_a
ammonium	ATf					225ᵃ	23.2
anilinium	AnTf	n.d.ᵇ	n.d	71.3	n.d	250ᵃ	18.6
ethylammonium	EATfᶜ	n.d	n.d	−12.9	172.1	312.1ᵃ	24.6
tert-butylammonium	tBATf	n.d	n.d	n.d	11.6	243.4ᵃ	24.7
2-fluoropyridinium	FPyTf	n.d	n.d	n.d	58.3	286	13.6
hydronium	H₃OTf	n.d	n.d	n.d	27.4	212.7	12.3
hydroxyethylammonium	HOEATf	n.d	−66	−1.6	74.8		26.9
methoxyethylammonium	MOEATf	n.d	n.d	n.d	n.d	283.5ᵃ	23.5
triethylammonium	TEATf	n.d	n.d	n.d	n.d	312.5ᵃ	24.7
1,2-dimethylimidazolium	DMImTf	n.d	n.d	n.d	115.3	298.9	22.4
imidazolium	ImTf	n.d	n.d	34	122.9	308.4	21.0
1-methylimidazolium	MImTf	45.8	56.7	78.6	92	323.5ᵃ	21.1

ᵃ Decomposes. ᵇ Not detected. ᶜ From differential scanning calorimetry data.

TABLE 8: Thermal Transition Temperatures for Methane Sulfonates

IL cation	symbol	T_g (°C)	T_m (°C)	T_{dec} (°C)	ΔpK_a
methylammonium	MAMS	n.d.ᵃ	91	260.2	11.2
ethylammonium	EAMS	n.d.	112.5	288.6	11.2
butylammonium	BAMS	−50	131.8	292.2	11.2
methoxyethylammonium	MOEAMS	n.d.	62.6	282.4	10.1
dimethylammonium	DMAMS	−95	122.1	278	11.4
dibutylammonium	DBAMS	−49	42.7	331.9	11.9
triethylammonium	TEAMS	−96.5	21.6	269.7	11.3
dimethylethylammonium	DMEAMS	n.d.	94.7	295.8	10.6

ᵃ Not detected.

Table 7, triflates (3 oxygens + perfluorinated methyl radical);

Table 8, methane sulfonates (3 oxygens + methyl radical);

Table 9, hydrogen sulfates (4 oxygens + H-bonders);

Table 10, fluorohydrogenphosphates (3 oxygens + 1 fluorine + 1 hydrogen bonder);

Table 11, dihydrogen phosphates (4 oxygens + two H-bonders);

Table 12, dianions:difluorides.

In the final column of each of Tables 3−12 we record the differences in pK_a values for the cation−anion combination ΔpK_a, based on aqueous solution measurements. These values are later used (in the Discussion section) for the construction of Gurney diagrams.

There are a small number of cases in which a glass temperature was recorded, but no subsequent crystallization and remelting was observed, suggesting that the liquid state is the stable state to very low temperatures relative to the glass temperature and hence is too viscous, when supercooled, to be able to nucleate any crystals. There are a much larger number of cases in which a melting point can be observed, but no glass transition is observed, because the liquid crystallized completely during cooling. In these cases the liquid is apparently very mobile at its melting point and has no problem in generating nuclei that then grow during cooling. For the majority of cases, both glass transitions and melting points can be measured. In these cases the two are approximately related by the "²/₃ law", as will be detailed in the discussion section.

The relation between these properties, the anion and cation structures, and the ΔpK_a values in Tables 3−12 will also be taken up in the Discussion section.

Densities. Although densities can be measured very precisely, high precision was not sought in this study. Rather, we used simple rapid techniques that yielded data of precision comparable to that of the log(conductivity) for the sole purpose of obtaining equivalent conductivities to construct Walden plots. Density and molar volume data are therefore not recorded here, but are available in Supporting Information and ref 26.

Ionic Conductivities. Ionic conductivity data are collected in Figures 4 and 5, which are representative rather than exhaustive.

The conductivities can be extremely high, from >150 mS·cm⁻¹ at 25 °C up to 470 mS·cm⁻¹ at 100 °C, as previously reported.[16] A variety of behavior is to be seen, which will be discussed below. Among the highest are some data from a 1970 study, which have previously only been available in a thesis.[27] The system in question is the monoprotonated salt of hydrazine and formic acid.

Viscosities. The viscosities measured on these liquids, shown in Figure 6 for the same representative series as in Figures 4 and 5 are generally high compared to water as reference substance, though several cases approach waterlike values, especially at high temperatures. Some of the highest conductivities are clearly related to exceptionally low viscosities, but this relation is not clarified until the data are compared in a Walden plot (see Discussion section).

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TABLE 9: Thermal Transition Temperatures for Hydrogen Sulfates

IL cation	symbol	T_g (°C)	T_c (°C)	$T_{S_1 \to S_2}$ (°C)	T_m (°C)	T_b (°C)	ΔpK_a
hydronium	H₃OHSO₄	−91.2[a]			8.5[a]	225[a]	7.3
ammonium	NH₄HSO₄	−65.6	−33	31.4	116.3	358.8[b]	18.2
methylammonium	MAHSO₄	n.d.[c]	n.d.	n.d.	73.2	302.3[b]	19.6
ethylammonium	EAHSO₄	−96.4	−54	n.d.	31.9	296.5[b]	19.6
propylammonium	PAHSO₄	n.d.	n.d.	n.d.	33.9	304.5[b]	19.6
butylammonium	BAHSO₄	−63.4	−19	n.d.	33.5	307.9[b]	19.6
tert-butylammonium	tBAHSO₄	n.d.	n.d.	n.d.	130.6	243.9[b]	19.7
dimethylammonium	DMAHSO₄	n.d.	n.d.	−61.1	40.1	310.9[b]	19.8
diethylammonium	DEAHSO₄	n.d.	n.d.	−43.3	77.3	301.5[b]	19.8
dibutylammonium	DBAHSO₄	n.d.	n.d.	16.7	130.9	283.5[b]	20.3
methylbutylammonium	MBAHSO₄	−79.6	−34.4	n.d.	42.2	285.8[b]	19.9
ethylbutylammonium	EBAHSO₄	n.d.	n.d.	−85.5	54.4	295.1[b]	19.8
trimethylammonium	TMAHSO₄	n.d.	n.d.	−77.7	72.9	308.9[b]	18.8
triethylammonium	TEAHSO₄	n.d.	n.d.	n.d.	84.2	262.8[b]	19.7
tributylammonium	TBAHSO₄	−57.1	−3.3	36.7	86.6	250.3[b]	19.0
dimethylethylammonium	DMEAHSO₄	−91.4	−34.1	n.d.	3.3	302.6[b]	19.0

[a] Reference 39. [b] Decomposes. [c] Not detected.

TABLE 10: Thermal Transition Temperatures for Fluorohydrogen Phosphates

IL cation	symbol	T_g (°C)	T_c (°C)	T_m (°C)	ΔpK_a
methylammonium	MAHPO₃F	−47.8	n.d.	n.d.	9.7
propylammonium	PAHPO₃F				9.8
butylammonium	BAHPO₃F	−50.1	n.d.	n.d.	10.7
dimethylammonium	DMAHPO₃F	−51.5	n.d.	n.d.	9.8
diethylammonium	DEAHPO₃F		n.d.	n.d.	9.8
dibutylammonium	DBAHPO₃F	−39.5	n.d.	75.7	10.3
dipropylammonium	DPAHPO₃F	−31.5	n.d.	n.d.	9.9
trimethylammonium	TMAHPO₃F	−44.5	n.d.	n.d.	8.8
triethylammonium	TEAHPO₃F	−59.7	n.d.	RTIL[b]	9.8
tributylammonium	TBAHPO₃F	−59.1	n.d.	RTIL[b]	9.0
tripropylammonium	TPAHPO₃F	−56.60	n.d.	30	9.0

[a] Not detected. [b] RTIL = room temperature ionic liquid.

Discussion

In this section we will comment on the relation of the observed physical properties to those measured in the wider fields of (i) aprotic ILs and (ii) glass-forming liquids in general. To commence, we consider the first-order phase changes, melting point and boiling point, and their relation to the internal cohesion indicator, T_g. This leads us to propose an energy level scheme within which the properties of these interesting liquids can be interpreted and which will later[21] be shown important for the interpretation of the properties of fuel cells containing these fluids as electrolytes. We discuss the transport properties, viscosity and conductivity, and their relationship to the ionicity of the liquids and to the possibility of "free" proton motion in electrolytes. The latter are all of importance to the possible applications of these liquids in such devices as fuel cells and photovoltaic converters. Finally we will examine how the protic IL fit into the overall "strong/ fragile" pattern of liquid viscosities, and how this may relate to the matter of "free" proton motion.

Melting Point−Glass Temperature Relations. It is common to relate the glass temperatures of glass-forming liquids to the melting points of the crystalline phase and obtain a linear relation with a slope close to 0.66 that has become known as the "²/₃ law" for glass transition temperatures. This rule seems to apply quite well to the present study when a limited group of salts, related by cation type, is considered (as illustrated in Figure 7). However, when all salts, for which we have both glass temperatures and melting points, are examined without discrimination, the scatter around the ratio ²/₃ becomes rather large, see Figure 8, and it becomes apparent that the ²/₃ law is not at all precise. Indeed, such imprecision is expected on general grounds.

The scatter would be considerably worse if we were to include data on samples of the easily crystallizing liquids, when they have been vitrified by hyperquenching or by small sample techniques.

The imprecision of the ²/₃ law stems from the circumstance that the "law" is not due to any link between glass relaxation and melting mechanisms and is not a law for glass temperatures but, rather, is a way of predicting which members of a series of systems for which both T_g and T_m are known, will be slow to crystallize at normal cooling rates. They will be those whose melting points are less than 50% above their glass temperatures. If their melting points are too low, then the liquids will never crystallize and we will not find out what those melting points are. We will only know that they are much less than 1.5 T_g and that special efforts, involving possibly high-pressure methods, will be needed to find their crystalline states. The formate of propylammonium cation ($T_m = -75$ °C) must have one of the lowest melting points yet measured for an ionic liquid.

What are the factors involved in causing melting points to be so low, relative to the forces that determine the viscosity and glass temperature? These have been discussed by many authors, and the present results are consistent with many of the ideas that have been presented. Shape factors that lead to low packing efficiencies are prevalent among these ideas, the concept being that irregular packing can sometimes have advantages over ordered packing for minimizing the energy. This seems to be particularly true when there is more that one type of interaction to deal with. For instance when both hydrogen bonding and shape accommodation must simultaneously be satisfied, then it is generally more difficult to optimize in ordered arrangements. Thus, the cases for which no crystals form, according to the DTA scans, often have −OH groups on the asymmetric cations (hydroxypropylaminium cation, for example, does not yield crystals with any anions of our study). Empirically, the more viscous the liquid is at melting point, the higher the glass-forming tendency. A current study on a monatomic glassformer[28] reveals that glass-forming propensities are maximized when the competing crystalline phases have the same energy and the structure of the liquid is distinct from that of either possible crystal.

That the glass transition temperatures for PILs are generally lower than those of aprotic ILs of the same nominal charge concentration (L/equiv) was demonstrated in an earlier paper,[16] and this rule seems to be upheld in this more extensive study.

Boiling Points and T_b/T_m Relations. The implication that the cohesive energy of the PILs is below that of the corre-

TABLE 11: Thermal Transition Temperatures for Dihdrogen Phosphates

IL cation	symbol	T_g (°C)	T_c (°C)	T_m (°C)	T_b (°C)	ΔpK_a
Hydronium	$H_3OH_2PO_4$			21	158	-3.9
ammonium	$NH_4H_2PO_4$	−23.3	10	193.3	376.1[a]	7.1
methylammonium	MAH_2PO_4	−28.8	22.5	96.8	254.2[a]	8.5
ethylammonium	EAH_2PO_4	−31.3	−5.8	109.5	346.4[a]	8.5
propylammonium	PAH_2PO_4	n.d.[b]	n.d.	145.6	315.3[a]	8.4
butylammonium	BAH_2PO_4	−33.3	2.2	113.3	275.7[a]	8.5
methoxyethylammonium	$MOEAH_2PO_4$	−20.3	44.3	90.5	278.6[a]	7.3
dimethylammonium	$DMAH_2PO_4$	−36.8	15.1	117.3	245.3[a]	8.7
diethylammonium	$DEAH_2PO_4$	−16.7	13.3	159	330.0[a]	8.7
dibutylammonium	$DBAH_2PO_4$	−15.6	n.d.	98	316.7[a]	9.1
methylbutylammonium	$MBAH_2PO_4$	−36	n.d.	38.7	320.1[a]	8.8
trimethylammonium	$TMAH_2PO_4$	−36.7	n.d.	n.d.	274.4[a]	7.7
triethylammonium	$TEAH_2PO_4$	−32.2	n.d.	n.d.	349.2[a]	8.6
tributylammonium	$TBAH_2PO_4$	−18.8	n.d.	n.d.	337.5[a]	7.9

[a] Decomposes. [b] Not detected.

TABLE 12: Thermal Transition Temperatures for Difluorides

IL cation	symbol	T_g (°C)	T_c (°C)	$T_{S_1 \rightarrow S_2}$ (°C)	T_m (°C)	T_b (°C)	ΔpK_a	ΔpK_0[a]
ammonium	NH_4HF_2	n.d.[b]	n.d.	−33.1	125.6	240[c]	6.0	24.3
methylammonium	$MAHF_2$	−104.1	−72.5	−29.9	−11.8	174.5	7.4	25.7
ethylammonium	$EA\ HF_2$	−100.3	−67	−16	3.5	176.4	7.4	25.7
dimethylammonium	$DMA\ HF_2$	−111	−64.6	−37.2	−22.9	178.4	7.6	25.9

[a] The pKa value for hydrofluoric acid is taken as its Hammett acidity function value, $H_0 = -15.1$. [b] Not detected. [c] Decomposes.
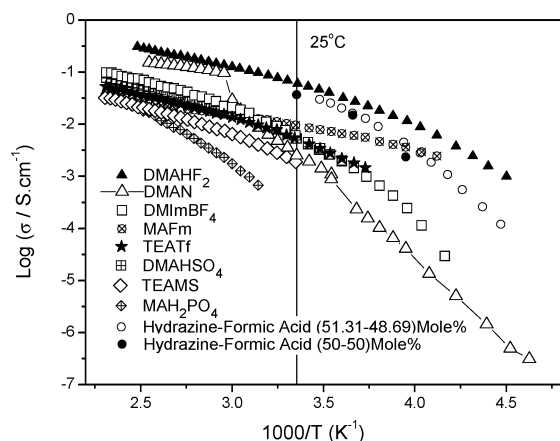
Figure 4. Ionic conductivities of a selection of the PILs from this study. In some cases, obvious from the breaks in the data, the conductivities of the crystalline states are included in the plot, as they have interesting high values.
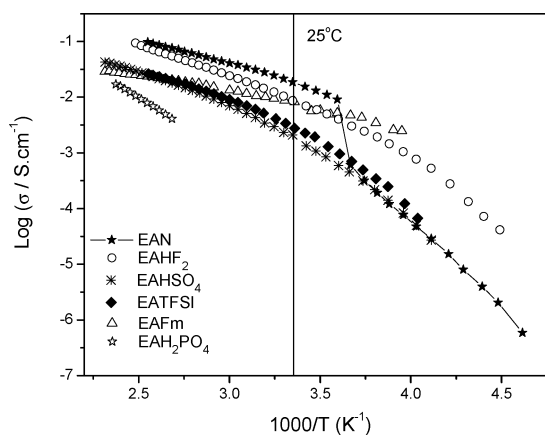

Figure 5. Ionic conductivities of PILs with a common cation (ethylammonium). The formate, with the weakest proton-transfer energy, shows distinct behavior.

sponding aprotic cases is supported by the boiling point data in Tables 3−12. Low T_g values generally correlate with low T_b values. Most of the salts that have high T_g values decompose before they can be observed boiling.

With molecular liquids, the boiling point/melting point ratio provides a reliable guide to glass-forming ability (GFA). Molecular liquids that boil at more than twice their melting points prove always to vitrify easily on cooling at normal rates. The present systems present an interesting test case here because, although the acid and base components are molecular liquids, their combination, on proton transfer, yields an ionic liquid in which the long-range coulomb forces might be expected to raise the boiling points sufficiently to invalidate the normal guide rule. The T_b/T_m ratio would then tend to exaggerate the GFA.

Although the majority of compounds reported here decompose before they boil, there are a number of cases in the Tables 3−5 where both boiling and melting points are available. For the formates, in which the proton transfer is not strongly driven (see below), the GFA is quite strong. This is predicted by the high T_b/T_m ratios, in some cases, but glasses also form in two cases where they are counterindicated by small (<2.0) ratios.

Thus the expected enhancement of the GFA for these cases is not borne out in practice. On the other hand, the same small ratio (1.79) correctly predicts the weak GFA in the case of ethylammonium nitrate, for which the T_g could only be obtained by extrapolation of binary solution data. The failure of the fluoroacetates to yield GF liquids is also consistent with the low T_b/T_m ratios found for these compounds. Overall, then, the ionicities of these liquids do not seem to have led to failures of the common phenomenological rules for glass formers. Perhaps the extent of proton transfer needs to be greater than it is in these cases for the rules to break down as they do, for instance, with the alkali halides. (The eutectic temperature in the LiCl−KCl system, 685 K, is much less than half the boiling point, but there is no GFA at all.) For the cases of more energetic proton transfer, we cannot test the rule because decomposition occurs before the boiling point is reached.

Boiling Points and Proton-Transfer Free Energy Relations. The boiling point of a protic IL is strongly dependent on the extent of transfer of the proton from the acid to the base. In earlier work,[8] we linked the boiling point excess (excess over the value expected from simple additivity of the boiling points of acid and base components) to the difference in pK_a values
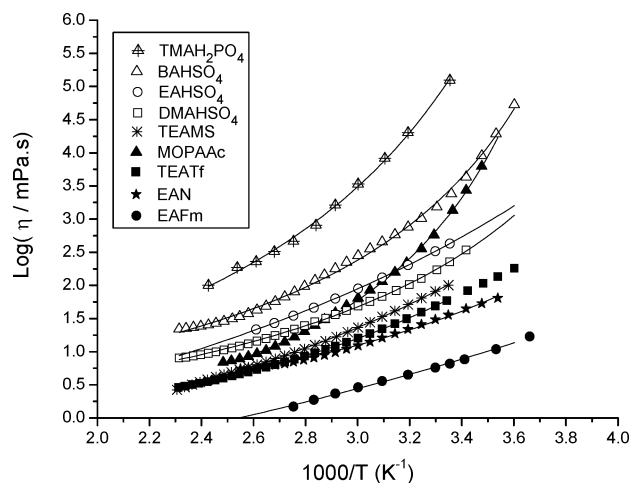
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Figure 6. Viscosities of a selection of the PILs studied in this work. Data on others are available as Supporting Information.
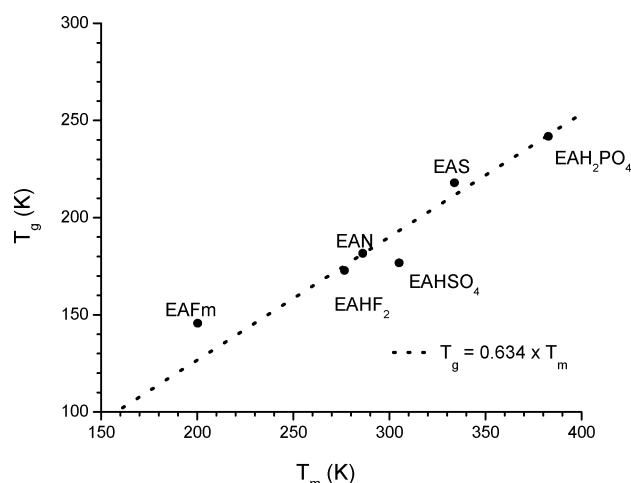

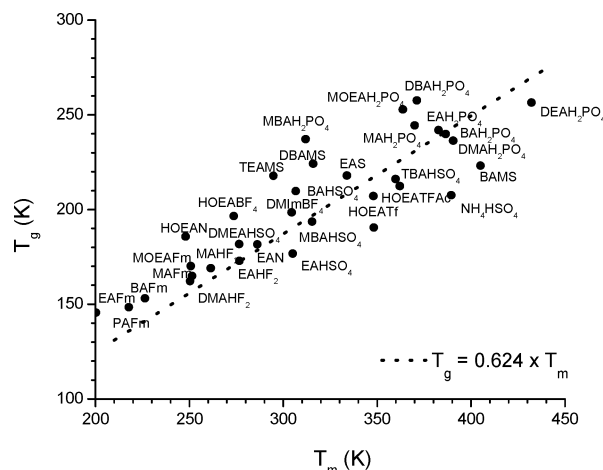**Figure 7.** Melting point in relation to glass temperature for PILs in the ethylammonium family.

Figure 8. Melting point vs glass temperature for all PILs.

Figure 9. The "excess boiling point" of PILs in relation to the difference in acid and base pK_a values, from aqueous solution data. Solid points and dashed line are from ref 8. A maximum in the excess boiling point in an acid + base binary system will correspond to a maximum deviation from ideal mixing in an isothermal vapor pressure vs composition plot for each of the acid and the base at that composition. This can be converted to a measure of the free energy change on transfer of the proton from acid to base in the dielectric medium established by the neat IL. $\Delta G^0 = -RT \Sigma \ln p_i/2p^0_i$ assuming this occurs at mole fraction $= \frac{1}{2}$. The quantity $2.303RT\Delta pK_a$ measures the free energy for the same process when the transfer occurs in the 1 M aqueous solutions. For strong monoprotic acids this will usually occur at the equimolar composition, though it may occur at higher X (acid) in cases where a strongly hydrogen-bonded dianion can form, as seen in an earlier study.[8]

for the acid and base of the proton-transfer couple. Each individual pK_a value relates to the free energy of transfer of a proton from the Brönsted acid to the water molecule by the expression

$$\Delta G^0 = -RT \ln K_a \tag{1}$$

where K_a is the acid dissociation constant.

So the free energy of transfer of the proton from acid to base, in an aqueous environment, is the sum of the two free energies, thus

$$\Delta G^0 \text{ (acid-to-base)} = -RT \Delta \ln K_a$$

$$= -2.303RT\Delta pK_a \tag{2}$$

Below, we will use this relation of ΔpK_a value to the free energy of formation of the salt from the original acid and base by proton transfer (after rationalizing its use in the absence of water) to construct a free energy level diagram for the acids and bases of this work. From such a diagram, many properties of yet-unsynthesized proton-transfer IL can be predicted. First, however, we reinforce its relevance to the boiling process, i.e., to the process in which the original proton transfer is thermally reversed to restore the original acid and base molecules at a total vapor pressure of 1 atm. In Figure 9, we reproduce the figure from ref 8 to which we have now added new data

acquired in the present study. The new data reinforce the earlier plot—so long as we restrict attention to proton transfers from acids to nitrogenous bases (which comprise the great majority of new data acquired in this study).

As seen before,[8] when the energy gap becomes larger than about 1 eV at 298 K, the boiling point becomes inaccessible because chemical decomposition (pyrolysis) occurs first. For those with less energetic proton transfers, the PILs can be evaporated under reduced pressure, and thereby purified or separated. They, and some unusual, strongly ion-paired aprotic IL cousins, have been called "distillable" ionic liquids.[29,30] On the other hand, protic ILs formed by proton transfers from superacids to strong bases behave like aprotic ILs.

It would be useful, in the future, to make direct vapor pressure measurements at lower temperatures (low vapor pressures) to clarify this domain of behavior (see also Figure 9 caption).

Gurney-Type Proton Free Energy Level Diagram for Proton-Transfer Systems. As indicated in the caption of Figure
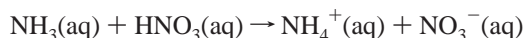
9., the free energy change due to transfer of the proton from acid to base could be obtained from the appropriate vapor pressure measurements and a detailed comparison could then be made with the value estimated from the aqueous environmental data. Until this is done, however, the only comparison we can make is for the isolated cases where the appropriate free energy of formation ΔG_f^0 data for acid, base, and proton-transfer salt, are available in the literature. Let us check one case to see how serious the difference is. We take the case of ammonium nitrate for which the free energies of formation for NH_3, HNO_3, and NH_4NO_3 are tabulated in standard references. In such a case the free energy of formation of the proton-transfer salt from the acid and base components at 298 K can be obtained simply as

$$\Delta G^0 = \Delta G^0(NH_4NO_3) - \Delta G^0(HNO_3) - \Delta G^0(NH_3)$$

which proves to be -86.7 kJ/mol.[31] We convert the proton-transfer energy to units of electron volts, $\epsilon = -\Delta G^0/F$ (0.90 eV, only one proton is transferred) as used by Gurney in construction of the proton free energy level diagrams in his classic 1953 book, *Ionic Processes in Solution*.[32] The proton energy gap is therefore 0.90 eV.

Since ammonium nitrate, for which the free energy of formation is tabulated, is a solid, and since we are interested primarily in cases in which the product is a liquid, the above value should be corrected to one appropriate for the less stable supercooled liquid. The correct gap must therefore be smaller than 0.90 V. By knowledge of the entropy of fusion of ammonium nitrate (which we have measured:[33] -13.2 J/ mol· K at 443 K), we can assess the difference in free energy of liquid and crystal at the lower temperature, 298 K. It is small, amounting to only 1900 J. Corrected, the free energy change per mole of transferred protons is -85 kJ, and the "proton energy gap" that is crossed in forming the IL becomes 0.88 eV. These values are to be compared with those obtained from the thermodynamic data available for the free energies of formation of ammonium and nitrate ions from $NH_3(aq)$ and $HNO_3(aq)$.

For the process

$$NH_3(aq) + HNO_3(aq) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

the data yield a free energy change ΔG^0 of -50.3 kJ/mol, or 0.52 eV per transferred proton, rather different from those for the "dry" process. The 0.36 eV difference is due to differences in free energies of solution (to 1 M in water) of the three components of the above reaction, starting from their standard states.

The pK_a-based relation, eq 2 above, should give the latter value, but use of pK_a values for acids and bases in 1 M aqueous solution tabulated in standard sources[34] yields a larger value, 68.1 kJ/mol or 0.71 eV. There seems to be some uncertainty about the pK_a value to be assigned to HNO_3. HNO_3 dissociation was discussed in detail by Gurney and if we use his value of pK_a in the assessment we obtain a proton gap of 0.57 eV.

The differences in "wet" and "dry" values for the proton-transfer gap warn us that, irrespective of correlations such as that of Figure 9, the estimation of proton-transfer gaps from pK_a data is only semiquantitative. Because we lack direct measurements based on thermodynamic data such as vapor pressures, we will proceed semiquantitatively, using the pK_a values available in the standard sources and also in SciFinder Scholar, to construct a free energy level diagram for proton-transfer salts which will prove useful for predicting not only
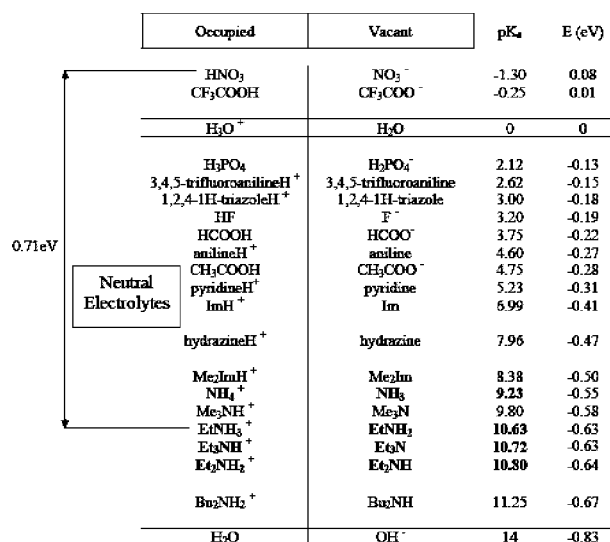
Occupied	Vacant	pK_a	E (eV)
HNO_3	NO_3^-	-1.30	0.08
CF_3COOH	CF_3COO^-	-0.25	0.01
H_3O^+	H_2O	0	0
H_3PO_4	H_2PO_4^-	2.12	-0.13
3,4,5-trifluoroanilineH^+	3,4,5-trifluoroaniline	2.62	-0.15
1,2,4-1H-triazoleH^+	1,2,4-1H-triazole	3.00	-0.18
HF	F^-	3.20	-0.19
HCOOH	HCOO^-	3.75	-0.22
anilineH^+	aniline	4.60	-0.27
CH_3COOH	CH_3COO^-	4.75	-0.28
pyridineH^+	pyridine	5.23	-0.31
ImH^+	Im	6.99	-0.41
hydrazineH^+	hydrazine	7.96	-0.47
Me_2ImH^+	Me_2Im	8.38	-0.50
NH_4^+	NH_3	9.23	-0.55
Me_3NH^+	Me_3N	9.80	-0.58
EtNH_3^+	EtNH_2	10.63	-0.63
Et_3NH^+	Et_3N	10.72	-0.63
Et_2NH_2^+	Et_2NH	10.80	-0.64
Bu_2NH_2^+	Bu_2NH	11.25	-0.67
H_2O	OH^-	14	-0.83

(Neutral Electrolytes; 0.71eV)

Figure 10. The proton free energy level diagram for ILs formed from moderately strong acid and moderately strong bases to yield neutral ionic liquid products. Arrows indicate the gap across which the proton falls in forming ethylammonium nitrate. Note that the value 0.71 eV is based on tabulated pK_a data and differs from the lower value, ~ 0.52 eV, suggested by free energy data for NH_4NO_3 (aq).

excess boiling points and ionicities but also performance as electrolytes in hydrogen/oxygen fuel cells. The energy level diagram is closely related to that constructed by Gurney for 1 M aqueous solutions.[32] In Gurney's case, the only approximation involved was that of treating a one molar solution as a standard state.

The diagram is presented in two versions, one in which the levels are quantitative with respect to pK_a, but of limited range, and a second one in which the total range of energies is much larger and the relative placement of levels less precise. The advantage of the larger scale diagram is that it allows us to see how the commonly discussed acid electrolytes and also basic electrolytes, that have been used for two common types of fuel cells in the past, relate to the "neutral" electrolytes that we are now able to synthesize in great variety. What we will show separately[20] is that when the electrolyte is formed by dropping the proton across a specially favorable "gap," the properties of the electrolyte may be optimal from the point of view of maximizing the open circuit voltage of the fuel cell near the theoretical value.

Gurney's basic approach of pairing occupied and vacant proton energy levels was introduced in our earlier paper on proton-transfer Ils,[8] and now we utilize it here without duplicate explanation. Figure 10 shows the energy levels for the HNO_3/NO_3^- and NH_4^+/NH_3 conjugate pairs separated by the energy gap based on the difference in HNO_3 and NH_4^+ pK_a values tabulated in the CRC Handbook ($\epsilon = 2.303RT\Delta pK_a$). The values assigned to each level are based on an assignment of $\epsilon = 0$ eV to the H_3O^+/H_2O level. The other common level, that for H_2O/OH^-, lies at -0.83 eV from the reference level, based on the relation $pK_a(H_3O^+) + pK_a(OH^-) = 14$ (thus $\epsilon = \Delta G^0/F = -2.303RT(14/96\,500) = -0.83$ eV).

Between these levels are placed others for the couples $HCOOH/HCOO^-$, ethylammonium/ethylamine, triethylammonium/triethylamine, etc., while shortly above the H_3O^+/H_2O level we place the levels for medium strong acids, HNO_3/NO_3^- and CF_3COOH/CF_3COO^-, using in every case the tabulated pK_a values to quantify the levels.

With these levels assigned, and subject to the above "wet" vs "dry" free energy provisos, we can now immediately obtain

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the proton-transfer energy involved in the formation of any ionic liquid that can result from combination of an acid in the left-hand column (an occupied proton level) with a base in the right-hand column (a vacant proton level), the proton-transfer resulting in the stable combination of anion and cation represented by the conjugate base and acid, respectively. [This uncertainty would be a much smaller value if the pK_a values could have been determined in an ideal solution state (a Henry's law standard state) in some particular ionic liquid solvent rather than in the usual aqueous solutions. This will be the subject of a separate publication (N. Byrne, J.-P. Belieres and C. A. Angell).] Thus we see that the formation of ethylammonium nitrate is accomplished by a proton falling across a gap of 0.71 eV or thereabout, which is close to the gap energy involved in the neutralization of H_3O^+ and OH^-. In the ethylammonium nitrate case, however, the resulting liquid consists of cations and anions, while in the case of water formation the product is a molecular liquid and an insulator.

Neutral Electrolytes vs Basic and Acidic Electrolytes. Ethylammonium nitrate, while highly ionic and conducting, has no acid or base properties, and relative to 1 molar acid or 1 molar base, it is a benign fluid. We call it a "neutral electrolyte" to distinguish it from a basic electrolyte, which is formed by transferring a proton from water to a strong base, e.g., to Na_2O to give the ionic product NaOH, which is highly corrosive when wet. Interestingly enough, according to the free energy change in the reaction $H_2O + Na_2O \rightarrow 2NaOH$, −143 kJ/mol, the proton crosses almost the same energy gap in forming "dry" NaOH as it does in the case of neutralization of 1 M strong acid with 1 M strong base, viz. 0.76 eV ($-\Delta G^0/2F$ because 2 mol of NaOH are produced). On the other hand, for NaOH(aq) the ΔG^0 value is more negative and the gap increases to 1.17 eV. For our purposes the "dry" value is the more appropriate. Thus the OH^-/O^{2-} level lies roughly the same distance below the H_2O/OH^- level as the latter lies below the H_3O^+/H_2O level. This is shown in the extended diagram, Figure 11.

We must note that the position of the OH^-/O^{2-} level on this diagram depends on how polarizing is the charge-compensating cation. By use of free energy of formation data, we obtain three levels for the three alkali metal cations Li^+, Na^+, and K^+. With Li^+, it falls at −0.54 eV, while for the less polarizing K^+ cation, it is lower, −1.03 eV. The properties of hydroxide solutions in which the alkali cations have been exchanged for weak field organic cations have not yet been explored to the best of our knowledge. Ionic liquid hydroxides presumably exist and they deserve study.

To understand the occurrence of decomposition before boiling in the case of PILs formed from superacids and strong bases, we need to add levels for the superacids to the energy diagram. To assign a level for triflic acid/triflate, we note that a pK_a of −14 has been assigned to triflic acid, based on the Hammett acidity function.[35] This leads us to place the HTf/Tf$^-$ level 0.83 eV above the H_3O^+/H_2O level. Thus when ethylammonium triflate is formed, the proton drops 1.46 eV. The thermal energy required to place this proton back on the triflate ion to reform the molecule greatly exceeds the thermal stability of the ethylammonium group, so no boiling is observable. This PIL is as ionic as any aprotic IL. For the case of transfer to the weak base fluoropyridine, however, the proton gap is only 0.90 eV, and a boiling point is observable.

Note that the protic ionic liquid generated by the proton transfer from triflic acid to water is hydronium triflate. On the basis of the ΔpK_a values, the proton gap is 0.83 eV, coincidentally the same as for H_2O formation and for NaOH

	Occupied	Vacant	pK$_a$	E (eV)
Acid Electrolytes	HSbF$_6$	SbF$_6^-$		
	HBOB	BOB$^-$		
	HTFSI	TFSI$^-$		
	HTf	Tf$^-$	-14	0.83
	HSO$_3$F	SO$_3$F$^-$		
	HClO$_4$	ClO$_4^-$	-10	0.59
	H$_2$SO$_4$	HSO$_4^-$	-9	0.53
	HPO$_2$F$_2$	PO$_2$F$_2^-$		
	HNO$_3$	NO$_3^-$	-1.30	0.08
	CH$_3$SO$_3$H	CH$_3$SO$_3^-$	-0.60	0.04
	2-fluoropyridineH$^+$	2-fluoropyridine	-0.43	0.03
	CF$_3$COOH	CF$_3$COO$^-$	-0.25	0.01
	H$_3$O$^+$	H$_2$O	0	0
Neutral Electrolytes	H$_3$PO$_4$	H$_2$PO$_4^-$	2.12	-0.13
	1,2,4-1H-triazoleH$^+$	1,2,4-1H-triazole	3.00	-0.18
	HF	F$^-$	3.20	-0.19
	HCOOH	HCOO$^-$	3.75	-0.22
	CH$_3$COOH	CH$_3$COO$^-$	4.75	-0.28
	ImH$^+$	Im	6.99	-0.41
	hydrazineH$^+$	hydrazine	7.96	-0.47
	NH$_4^+$	NH$_3$	9.23	-0.55
	EtNH$_3^+$	EtNH$_2$	10.63	-0.63
	Bu$_2$NH$_2^+$	Bu$_2$NH	11.25	-0.67
	H$_2$O	OH$^-$	14	-0.83
Basic Electrolytes	NH$_3$	NH$_2^-$		
	OH$^-$	O^{2-}(Na$^+$)	28	-1.66

Figure 11. Full proton free energy level diagram, showing the levels between which the proton falls in forming acid electrolytes as well as those between which it falls in yielding the basic electrolytes of familiar fuel cells.

formation. The actual gap is likely lower, based on boiling point observations (see below). It is a remarkable observation, though, that NaOH concentrated aqueous solutions, hydronium triflate and its solutions in excess water, and ethylammonium nitrate, when used as electrolytes in fuel cells, all yield cells that have the theoretical open circuit voltage for the H_2/O_2 reaction producing water. In a separate paper we will examine the question of whether or not this is just coincidence.

Nitrogenous vs Oxygenous Bases. It might be expected from the latter observations concerning the proton gap that the excess boiling point for hydronium triflate would be similar to that found for ethylammonium nitrate and its cousins. To our surprise this proves not to be the case. In the four studied instances of proton transfers to the water molecule, the excess boiling point can be measured, and the increase in boiling point is smaller than for the nitrogenous base cases of equal ΔpK_a values. With only four points and considerable scatter, a figure is unwarranted, but whatever the reason, it is clear that the stabilization of the liquid against reversion to the original base and acid molecular liquids is much smaller with oxygenous bases than is indicated by the tabulated ΔpK_a values.

Transport Properties and Ionicity

We now turn to the transport properties, conductivity, and fluidity. Generally speaking the liquids with high conductivities are also those with high fluidities, indeed this would be expected from the Walden rule connecting the charge mobility to the frictional resistance to its motion offered by the liquid viscosity, η. We have used the plot of log Λ vs $-\log \eta$ (i.e., log $\emptyset$, where $\emptyset$ is the fluidity) in a number of previous papers to classify ILs into ideal, subionic, and superionic cases, with most interest residing in the latter.
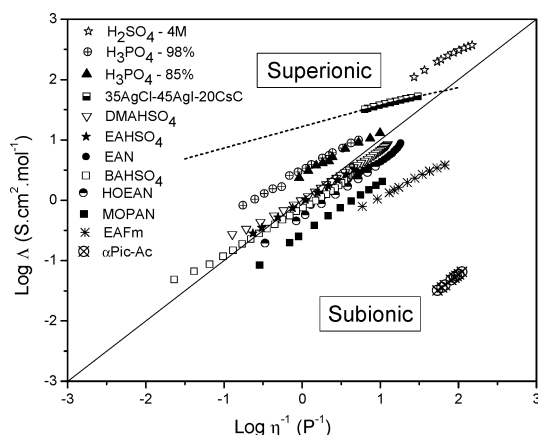
Figure 12. Walden plot for a selection of ILs of this study, for α-picolinium acetate from ref 8 and for a silver ion superionic from ref 16.
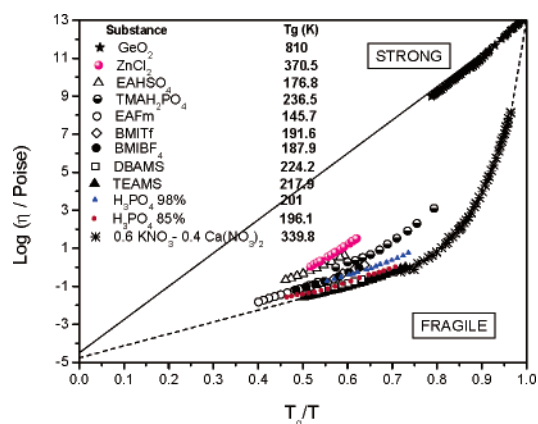

Figure 13. Fragility plot for a selection of ILs of this study. Note the presence of the dihydrogen phosphates, which support superprotonic conductivity, in the intermediate fragility domain. Hydrated phosphoric acid, the best free proton conductor, is however, not an intermediate liquid in this scheme.

One of the hopes for this study was that, by covering a broad enough range of systems, cases in which the transferred protons would find ways of moving through the fluid independently of the bulkier anions and cations might emerge. Certainly a "dry" proton conductivity mechanism is one of "holy grails" of electrolyte science. Such cases could be revealed by means of the classical Walden plot, "dry" proton motion being indicated by data points in the "superionic" domain of the diagram above the diagonal line of unit slope. So far we have little indication of such a mechanism, though it does seem to be significantly present in the case of phosphoric acid, especially at very high concentrations where the standard Grotthus mechanism that acts in the case of dilute aqueous acids has been largely suppressed by breakdown of the water network.

Walden plots for a number of cases from the present study are shown in Figure 12. Some data for phosphoric acid of high concentration and sulfuric acid at low concentration are included as examples of superionic behavior. We note that the mole ratio of water to phosphoric acid is very close to unity in the 85 wt % H_3PO_4 solution. If there were a substantial proton energy level gap between $H(H_2PO_4)/H_2PO_4^-$ and H_3O^+/H_2O, then 85% H_3PO_4 would be hydronium dihydrogen phosphate, but in fact the gap is negative. The subject of such acidic solutions, as opposed to PILs, will be dealt with in a separate paper.

While superionic conductivity is regrettably not in evidence in the protic ILs of the present study, the opposite case of

"subionic" conductivity is abundantly illustrated. For any case in which the proton-transfer energy, according to Figure 11, is less than 0.5 eV, we find conductivities well below the ideal line of Figure 12. They did not yield the conductivity expected from their high fluidities because on average the proton transfer is incomplete.

They behave as if there is only a small population of ions and the "ionicity" of the liquid is therefore reduced, i.e., the liquid is subionic. Data from a subset of the cases studied are shown in Figure 12 to illustrate this point. It was shown in Figure 10 of our previous paper[8] that the deviation from Walden ideality varies very strongly with ϵ at low ϵ but then flattens out and becomes insignificantly different from the ideal value for any $\Delta pK_a > 8$ ($\epsilon > 0.5$ eV). The present study confirms this finding but adds little to it. It is confirmed, then, that for purposes of electrical conductivity, any moderately large ϵ (>0.6, suffices to give IL conductivity) but low vapor pressure requires the largest possible proton energy gap. The volatility of low-gap PILs has been noted in other recent publications.[29,30] The present article provides a basis for predicting the volatility in individual cases.

Fragility of PILs. Finally we return to the starting point of this article to ask where the liquids of this study fall in relation to the simple molten salts, including many aprotic ILs, with respect to the important liquid-state property, fragility, i.e., where do they fall in the overall hierarchy of configurational excitability. Although we have not made viscosity measurements over a very wide range, there are enough data to provide an adequate idea of their range of behavior.

In Figure 13, we plot the data for the present liquids within a frame provided by the most, and least, fragile of the aprotic ILs. We include one "intermediate" case, that of the dense (as opposed to open) network liquid, zinc chloride. It can be seen that the PILs cover the spectrum from intermediate to very fragile, with strong representation in the intermediate range from the cases with acid anions.

These are the cases which have greatest hydrogen-bonding contributions to their interparticle interactions and which will therefore tend to have most extended intermediate range order. Intermediate range order is a characteristic associated with low fragility. Perhaps not surprisingly, the dihydrogen phosphates are also the cases in which evidence for superprotonic behavior is strongest (see Figure 12).

Concluding Remarks

The protic subclass of ILs is enormously broad, and we have only touched on the most obvious examples. There is a very large group of PILs with benign and even edible cations, and complimentary anions, with biologically interesting possibilities waiting to be explored. It is common knowledge that many pharmaceutical preparations are marketed as "hydrochlorides". These are proton transfer salts chosen for their high melting points. Many would become PILs if the chloride anion was replaced by thiocyanate or trifluoroacetate. On the other hand, there is a smaller field of inorganic protic ILs some members of which have proven of great interest as electrolytes for fuel cells.[40] While examples of single component inorganic protic salts with melting points below 100 °C (like hydrazinium nitrate ($T_m = 70$ °C)[27,41] may be rare, mixtures of such salts are frequently liquid in the IL range, and their stabilities, in the case of large proton transfer energies, may be important.[40]

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Supporting Information Available: Density and molar volume data and viscosities of some PILs studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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Binary inorganic salt mixtures as high conductivity liquid electrolytes for >100 °C fuel cells†

Jean-Philippe Belieres,[a] Don Gervasio[b] and C. Austen Angell*[a]

We report the successful application of low-melting inorganic salts with protonated cations (*e.g.* ammonium) as electrolytes in fuel cells operating in the temperature range 100–200 °C, where even with unoptimized electrodes, cell performance is comparable to that of the phosphoric acid fuel cell operating with optimized electrodes in the same temperature range, while open circuit voltages, and efficiencies at low current densities, can be much better—and there is no need for humidification or pressure to sustain performance.

Over the past two decades there has been a surge of interest in the use of "ionic liquids" as room temperature solvent media of low vapor pressure in which chemical reactions can be carried out without need for control of toxic vapors.[1] Many other useful applications for these media have also been discovered.[2,3] Most recently[4–10] interest has turned to the use of liquids in which the cations are formed by proton transfer, because they tend to be more fluid than the aprotic cases,[8] hence more conductive. In particular, they can also be used as proton transfer media in fuel cells and other electrochemical devices.[6,7,9–11] The possible function of solvent-free ionic liquids as fuel cell electrolytes was first reported by Susan *et al.*,[6] though the use of imidazole and related molecules as proton carriers in polymeric membrane electrolytes had begun in 1998.[12]

In this laboratory we have shown that when ethylammonium nitrate is used as the electrolyte, the cell suffers almost no polarization at the oxygen electrode.[7,9] The result is that the cell voltage closely approaches the theoretical value of 1.15 V at 150 °C. However, we find that the cell lifetime is limited, probably because of C–H bond cleavage in the presence of the platinum catalyst. In the present communication we show that the large organic cation is by no means necessary for the fuel cell electrolyte function. Indeed for purposes of high current density cells, the removal of the organic component seems to bestow an advantage. Here we detail several low melting or low liquidus temperature inorganic ionic liquids and then exemplify their performance in fuel cells by comparing with the performance of the phosphoric acid fuel cell.

Inorganic ionic liquids, in the current sense of ionic compounds that are liquid below 100 °C, are not abundant. Some examples were provided in a recent review.[9] When proton transfer salts are included, the list expands. The low melting points of binary melts

[a]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA. E-mail: caa@asu.edu; Fax: +1 480 965 2747; Tel: +1 480 965 7217*
[b]*Center for Applied NanoBioscience, Arizona State University, Tempe, AZ 85287, USA*

† The HTML version of this article has been enhanced with colour images.

containing ammonium salts have long been known to molten salt chemists. The eutectic temperature of 98 °C for $LiNO_3$–NH_4NO_3, for instance, has been known since 1962[13] and its glass temperature was reported in 1971.[14] The inorganic proton transfer salt hydrazinium nitrate, T_m = 70 °C,[15] satisfies the current definition of an "ionic liquid" (melting below 100 °C), and its binary solutions with other hydrazinium salts (and certain ammonium salts also) must have eutectic melting points that are sub-ambient. Because we wish to ensure high temperature stability and to maximize the concentration of proton carriers, we will focus on ammonium salts and their mixtures. The only mention we find of ammonium salts serving as a component of a fuel cell electrolyte is that of Matsui *et al.*[16] where a complex phosphate combination NH_4PO_3–TiP_2O_7 was used at 250 °C. However, the ammonium compound involved is a *meta*phosphate, so the anion is an infinite chain of $[PO_4]$ tetrahedra, and comparison with the simple salts used in our work is hardly appropriate.

Using differential scanning calorimetry to detect the thermal events during heating, we have determined complete phase diagrams for three binary ammonium salt systems ((1) trifluoromethanesulfonate ("triflate", Tf) + trifluoroacetate (TFAc), (2) trifluoroacetate + nitrate, and (3) triflate + nitrate), and find simple eutectic behavior in each case.

The first system has a eutectic temperature of 69 °C, amounting to a freezing point lowering of some 50 °C from the T_m of the lower-melting of the two salts. The second, NH_4TFAc + NH_4NO_3, was expected to have an even lower eutectic temperature but this proves not to be the case. The phase diagram for this system, which proves one of the most suitable for our fuel cell purposes, is shown in Fig. 1. The melting points of a variety of other ammonium salts are listed in Table 1, and eutectic temperatures for some additional pairs are also listed.
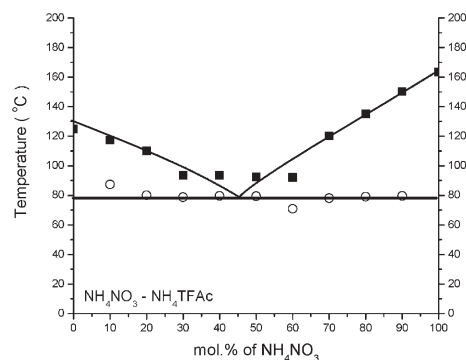

Fig. 1 Phase diagram of the system ammonium nitrate + ammonium trifluoroacetate. The eutectic temperature lies at 79 °C.

Table 1 Thermal properties of several ammonium salts

Salt and anion formula	$T_m/$ °C	$T_e/$°C (with…)
Ammonium triflate (Tf) $CF_3SO_3^-$	225	104(NH_4NO_3)
" trifluoroacetate (TFAc) CF_3COO^-	125	69 (NH_4Tf)
Ammonium tetrafluoroborate BF_4^-	230	160 (NH_4Tf)
" methanesulfonate CH_3SO_3-	183	
Ammonium nitrate NO_3^-	169	79(NH_4TFAc)
Ammonium thiocyanate SCN^-	153	72(NH_4TFAc)
Ammonium sulfamate $SO_3NH_2^-$	133	
Ammonium bifluoride HF_2^-	125	
Ammonium hydrogen sulfate HSO_4^-	116	
Ammonium bis(trifluoromethanesulfonyl)imide (TFSI) $(CF_3SO_2)_2N^-$	178	103 (NH_4Tf)
Ammonium bis(perfluoroethanesulfonyl)imide (BETI) $(CF_3CF2SO_2)_2N^-$	237	107 (NH_4Tf)
Hydrazinium nitrate[15]		70

The conductivities of these melts are very high compared with those of most aprotic ionic liquids. Fig. 2 presents data in the form of an Arrhenius plot where comparison is made with that of ethylammonium nitrate presented in earlier work.[8] At 150 °C the conductivities, many of which reach values of 100 mS cm^{-1}, are comparable to those of aqueous solutions. Included in Fig. 2 are data for two phosphoric acid solutions of different water contents (85 wt% H_3PO_4 closely approximates the stoichiometry $[H_3O^+][H_2PO_4^-]$) which are higher-conducting because of their protonic acid character.

Using in-house Teflon sandwich fuel cells that are described elsewhere,[17] we have determined the current flowing under load when E-TEK electrodes are utilized. Results are shown in Fig. 3. The upper curve shows the remarkably high voltage output of cells using electrolytes containing ethylammonium nitrate EAN, particularly when the EAN is doped with 1% ethylammonium dihydrogen phosphate to reduce its wetting of the E-TEK electrode. Unfortunately, the electrode wetting problem is not really solved and accordingly, these currents are not maintained at high load, relative to those produced by the phosphoric acid cell.

By contrast, in cells using the binary ammonium salts (NH_4Tf + NH_4TFAc) eutectic as electrolyte, the current at high load is maintained in a manner comparable to that of the phosphoric acid cell. However, in this case the open circuit voltage is poor.

In view of the exceptional voltage output of the ethylammonium nitrate fuel cell, it has been natural to test inorganic electrolytes
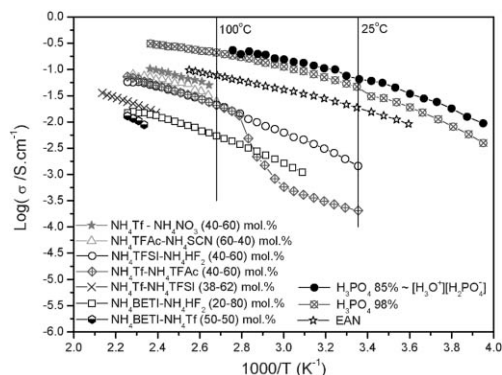
Fig. 2 Arrhenius plot of conductivities of ammonium salt mixtures. Comparison is made with EAN and two phosphoric acids of different water content. High conductivity in solid state is shown for one case.
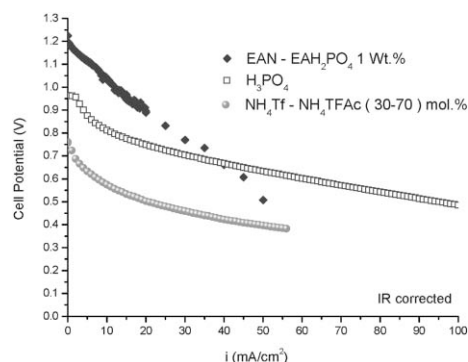
Fig. 3 Total polarization curves for fuel cell with NH_4Tf–NH_4TFAc electrolyte, in comparison with those for phosphoric acid and dihydrogenphosphate-doped ethylammonium nitrate,[17] all measured in the same cell. The curves have been IR corrected. Anode and cathode are ETEK platinum catalyzed porous gas fed electrodes with Pt-loading = 0.5 mg cm^{-2}. Anode feed: hydrogen. Cathode feed: oxygen.

with ammonium nitrate components. These were subjected to careful pre-tests for explosion potential, and were found to be surprisingly stable, indeed they resisted all attempts to destroy them. The cell using the equimolar NH_4NO_3 + NH_4TFAc electrolyte proves to be the most stable of all electrolytes yet tested, yielding invariant potential at fixed load, day after day of cell use. The cell using 60 : 40 NH_4NO_3 : NH_4Tf yields a very high open circuit voltage, 1.20 V. This exceeds the theoretical voltage 1.15 V
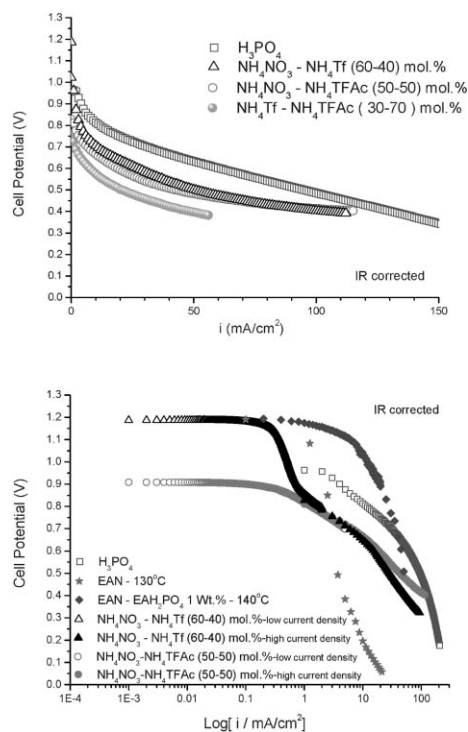
Fig. 4 (a) IR-corrected polarization curves for cells using (1) ethylammonium nitrate, (2) ethylammonium nitrate doped with 1 wt% ethylammonium dihydrogen phosphate, (b) the two inorganic binary salts containing the nitrate anion, shown in the Tafel plot form, cell voltage vs. log current density. Overlap of data from independent runs using different current range instruments, establishes reproducibility of behaviour. Plateau implies ideal (barrier-free) reduction at low current.
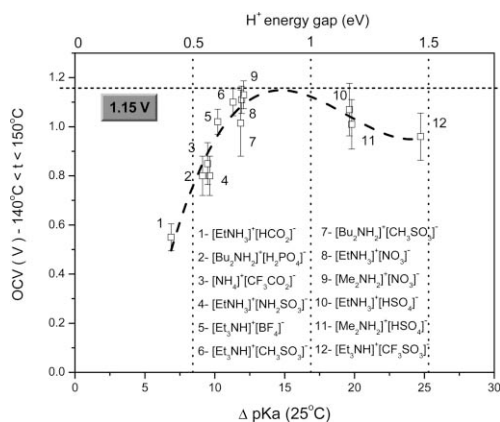
Fig. 5 Open circuit cell voltages in relation to the proton transfer energy gap characterizing the protic ionic liquid electrolyte, showing the range of electrolytes that can yield theoretical fuel cell voltages (see ref. 17 for details).

at 150 °C, due to the low product water activity. Unfortunately, this extraordinary voltage is not maintained under load. These and a number of additional cases are shown in Fig. 4a. The results for selected cases are shown in the Tafel plot form, cell voltage *vs.* log current density, in Fig. 4b. The plateau at 1.20 V in the case of NH_4Tf–NH_4NO_3 is particularly striking, signifying ideal barrier-free electroreduction. The reason that the voltage drops abruptly at current densities above 0.5 mA cm^{-2}, but then resumes at a lower cell voltage, must have to do with on-catalyst absorption[18] and will obviously become the focus of future research. A cell that could maintain a 1.1–1.2 V output in the way that the lower voltage outputs of Fig. 4a are maintained, would be an exciting development in fuel cell technology.

Cell voltages in the range 1.15–1.2 V are not confined to nitrate anion-containing ionic liquids. In work being published in detail elsewhere,[17,19] we have shown that this level of open circuit voltage seems to be common to protic ionic liquids that are formed by transfer of protons across a free energy gap of about 0. 6–1.0 eV. To support this assertion, we reproduce from the more detailed publication a key figure showing the relation between measured fuel cell OCV and the proton energy gap between donor acid and acceptor base of the protic electrolyte which, by unproven assumption, is proportional to the aqueous solution metric ΔpK_a. ($\Delta G_{(proton\ transfer)} = -2.303RT\Delta pK_a$). Conditions under which this assumption can be justified, are discussed elsewhere.[20] A theoretical account of the Fig. 5 correlation is not available at this time. The plot suggests that there will be many protic salts which, used as liquid electrolytes, will yield high fuel cell OCV values.

Finally we should note an additional advantage of the type of fuel cell that this research reveals. Where conventional water-based proton transfer electrolytes (either with water as base, meaning acid electrolytes, or with water as acid, meaning basic electrolytes) are intrinsically corrosive and demand noble metal catalysts, the electrolytes of the present work can be neutral,[20] while still highly conducting and effective as proton carriers. Their benign character not only simplifies cell construction but also opens the door to many alternative catalysts, including heat-stable enzymes, indeed any catalyst that might aid in the oxygen reduction process.

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Parallel Developments in Aprotic and Protic Ionic Liquids: Physical Chemistry and Applications

C. AUSTEN ANGELL,* NOLENE BYRNE, AND JEAN-PHILIPPE BELIERES

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

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ABSTRACT

This Account covers research dating from the early 1960s in the field of low-melting molten salts and hydrates,which has recently become popular under the rubric of "ionic liquids". It covers understanding gained in the principal author's laboratories (initially in Australia, but mostly in the U.S.A.) from spectroscopic, dynamic, and thermodynamic studies and includes recent applications of this understanding in the fields of energy conversion and bio-preservation. Both protic and aprotic varieties of ionic liquids are included, but recent studies have focused on the protic class because of the special applications made possible by the highly variable proton activities available in these liquids.

In this Account, we take a broad view of ionic liquids (using the term in its current sense of liquids comprised of ions and melting below 100 °C). We include, along with the general cases of organic cation systems, liquids in which common inorganic cations (like Mg^{2+} and Ca^{2+}) strongly bind a hydration or solvation shell and then behave like large cation systems and melt below 100 °C.

Austen Angell obtained his bachelor's and Masters' degrees from the University of Melbourne, Australia, and his Ph.D. from Imperial College of Science, University of London. He is currently Regents' Professor of Chemistry at Arizona State University, Tempe, AZ, having moved to ASU in 1989 after 23 years at Purdue University. His first work in the sub-100 °C ionic liquids field was done at Melbourne University. He has since worked on a wide range of problems related to liquids and glasses, including electrolytes for lithium batteries and most recently ionic liquids for fuel cells and protein folding/preservation studies. He has been especially intrigued by the problem of supercooled water and related liquids in which the phenomenon of polyamorphism is encountered. Awards for research have included the MRS Turnbull Lecture (2006), ACS Joel Henry Hildebrand award for the study of liquids (2004), the Neville Mott award of the *Journal of Non-Crystalline Solids* (1992), and the Morey award of the American Ceramic Society (1990). He has also been the recipient of an Alexander von Humboldt senior research award, and a Fulbright award. He has served on the editorial boards of a number of major journals including the *Journal of Physical Chemistry*, the *Journal of Chemical Physics*, and *Annual Review of Physical Chemistry*. In 1998, he was honored with a special issue of the *Journal of Physical Chemistry*.

Nolene Byrne received her B.E.(Mat)(Hons) in 2003 then a Ph.D. in 2006 from Monash University, Australia, in the area of improved electrolytes for lithium metal batteries. She is currently in a postdoctoral role at Arizona State University, Tempe, AZ. Her research involves the use of ionic liquids as media for improved biopreservation and electrochemical devices.

Jean-Philippe Belieres did his undergraduate studies at the Université Joseph Fourier in Grenoble, France, and his Master degree in electrochemistry at the Institut National Polytechnique de Grenoble, France. He received his Ph.D. in Chemistry from Arizona State University, and he is currently a Research Assistant Professor in the Chemistry and Biochemistry department at ASU. His research has been focused on fuel cells, lithium batteries, and ionic liquids.

We will try to organize a wide variety of measurements on low-melting ionic liquid systems into a coherent body of knowledge that is relevant to the ionic liquid field as it is currently developing.

Under the expanded concept of the field, ionic liquid studies commenced in the Angell laboratory in 1962 with a study of the transport properties of the hydrates of $Mg(NO_3)_2$ and $Ca(NO_3)_2$. These were described as melts of "large weak-field cations"[1] and their properties correlated with those of normal anhydrous molten salts via their effective cation radii, the sum of the normal radius plus one water molecule diameter. This notion was followed in 1966 with a full study under the title "A new class of molten salt mixtures" in which the hydrated cations were treated as independent cation species. The large cations mixed ideally with ordinary inorganic cations such as Na^+ and K^+, to give solutions in which such cohesion indicators as the glass transition temperature, T_g, changed linearly with composition. The concept proved quite fruitful, and a field ("hydrate melts" or "solvate melts") developed in its wake in which asymmetric anions like SCN^- and NO_2^- were used with solvated cations to create a very wide range of systems that were liquid at room temperature, while remaining ionic in their general properties.

The validity of the molten salt analogy was given additional conviction by the observation that transition metal ions such as Ni(II) and Co(II) could be found in the complex anion states $NiCl_4^{2-}$ and $CoCl_4^{2-}$ when added to the "hydrate melt" chlorides.[2]

Of special interest here was the observation[3] of extreme downfield NMR proton chemical shifts of hydrate protons when the hydrated cation was Al^{3+}. These lay much further downfield than did the protons in strong mineral acids at the same concentration, leading to the design of solutions of highly acidic character from salts that would usually be considered neutral. Indeed it was shown in ref 3 that platinum can be dissolved much more rapidly in a hot ionic liquid formed from $AlCl_3 \cdot (H_2O)_6 + Al(NO_3)_3 \cdot (H_2O)_{12}$ than in boiling aqua regia. This scenario of variable proton activity in solvent-free, nominally neutral ionic liquids will be revisited in the context of protic ionic liquids at the end of this Account.

Most of the interest in the field lies with room temperature liquids in which the cations are indeed of organic origin, and the story takes up naturally with these because of the manner in which the organic cation ionic liquids can be put to use in providing excellent complex anions for spectroscopic study. A good example is that shown in Figure 1 from the work of Gruen and McBeth[4] in whose laboratory one of us first encountered melts such as pyridinium chloride, PyHCl, and first used them in the (unpublished) study of Ni(II) complexes in low-melting systems such as PyHCl–$ZnCl_2$. We were impressed by the sharp changes in electronic spectra of Ni(II), reflecting
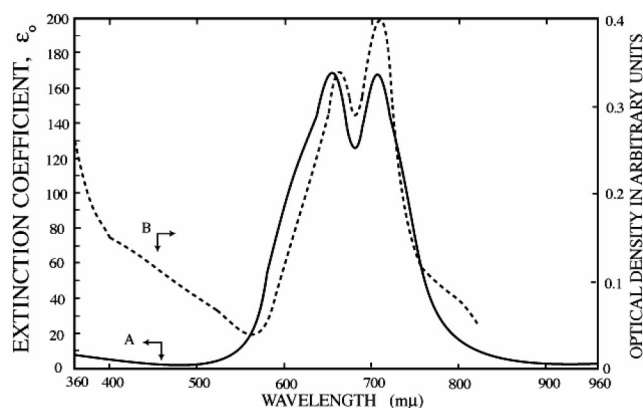
FIGURE 1. Electronic (visible) spectrum of Ni^{2+} dissolved at 10^{-4} mol/L in pyridinium chloride. Reprinted with permission from ref 4.

distinct and different structures, which were produced by small changes in solution composition.

The knowledge that these liquids could be used for molten salt studies at low temperatures quickly became useful when the new science of high-pressure physical chemistry using the diamond anvil high-pressure cell (DAC) burst on the scene. Little was known at that time of the effect of pressure on ion coordination.

The DAC was then only available for room-temperature studies, and a room-temperature molten chloride for the application of this newly invented high-pressure technique was needed. Even these days, ambient-temperature ionic liquid chlorides are not common, but Angell and Abkemeier[5] found that ethanolaminium chloride could serve as the ambient-temperature noncrystallizing component that induced ambient-temperature stability on mixtures with ethylammonium chloride. This chloride ion melt proved ideally suited for the study of transition metal ion spectra up to 3.5 GPa, pressure being calibrated in the range to 0.3 GPa by observing the glass transition spectroscopically and relating it to independently determined T_g values from high-pressure differential thermal analysis (DTA) studies.

Ni(II) electronic spectra of good quality, shown in Figure 2, were obtained, and the conversion from $NiCl_4^{2-}$ at ambient pressure to $NiCl_6^{4-}$ at higher pressures was observed. Impressively simple, the change with pressure of the equilibrium constant

$$d\ln K_{eq}/dP = -\Delta V/RT \qquad (1)$$

for the process $NiCl_4^{2-} + 2Cl^- \rightarrow NiCl_6^{4-}$, yielded a ΔV within 10% of the volume of 2 mol of chloride ion.[5]

Role of Complex Anions in the Development of Ambient Temperature Air- and Water-Stable Ionic Liquids

While the latter study of transition metal spectra used organic cation ionic liquids as a tool for the study of complex ions, Hodge and co-workers[6] used complex anions in organic cation salts for the study of ionic liquid properties, indeed properties that have found recent applications.

The dramatically different effects of complexation on the liquid viscosity are well illustrated by a 1976 study[6] that used the lower-melting α-methyl derivative of pyridinium chloride as the source of the Lewis base chloride. Data seen in Figure 3 show that the cohesive energy of an ionic liquid is lowered most strongly when chloride ions are complexed by $FeCl_3$ to produce the large singly charged $FeCl_4$ anion. This observation leads to the prediction that, among ionic liquids of a given cation, the tetrachloroferrate salt should be the most fluid and also most conductive, even more so than the well-studied ionic liquids containing $AlCl_4^-$ anions.[7] The veracity of this expectation is demonstrated in Figure 4 for salts of the butylmethylimidazolium cation taken from a very recent study by Xu et al.[8] For the 25 °C conductivity, the tetrachloroferrate is half an order of magnitude above any others in the group. The increase of ionic mobility by complexation seen here is no different in principle from the use of BeF_2 additions to alkali fluoride melts utilized in the molten salt reactor technology that had provided much of the driving force, and also funding, for molten salt studies in the 1950–1970 period. There, the addition of 1 mol of BeF_2 replaced two high charge intensity fluoride anions with a doubly charged anion of much larger dimensions, for a net decrease in cohesion.

The fluorinated anion salts (containing BF_4^- and PF_6^-) that are most frequently cited in connection to practical applications of the ambient-temperature ionic liquids, are to be understood in the same terms (unfortunately, the tetrachloroferrate anion is slowly hydrolyzed by water, and the applications of ambient temperature ionic liquids generally require the presence of water-stable anions). Fluorinated species in addition to being water-stable have the advantage of being unpolarizable and so minimize the effect of van der Waals contributions to the liquid cohesion. The importance of this characteristic of fluorinated anions to ionic liquid properties was first emphasized in a 1983 study of binary solutions of ionic liquid halides with lithium halides by Cooper.[9] There it was predicted that the replacement of iodide anions by the equivalent number of BF_4^- anions would lead to an increase of ambient temperature conductivity, which was then proven true (unfortunately only in a "note added in proof" in ref 9) by some 2 orders of magnitude.[9,10] Cooper's further extensive syntheses and measurements on viscosity and conductivity of a family of tetraalkylammonium tetrafluoroborate salts remained unpublished (for over 2 decades) until 2003.[8]

In the meantime, Cooper and O'Sullivan[11] reported, in 1992, the first systematic study of ambient-temperature water-stable ionic liquids, using triflate and related anions combined with imidazolium type cations. This announcement, presented at one of the Electrochemical Society's International Molten Salt Conferences and eventually published in its proceedings,[11] was immediately followed by a communication by Wilkes and co-workers[12] who had been working on similar salts, and the field of high-fluidity, water-stable ionic liquids was launched.
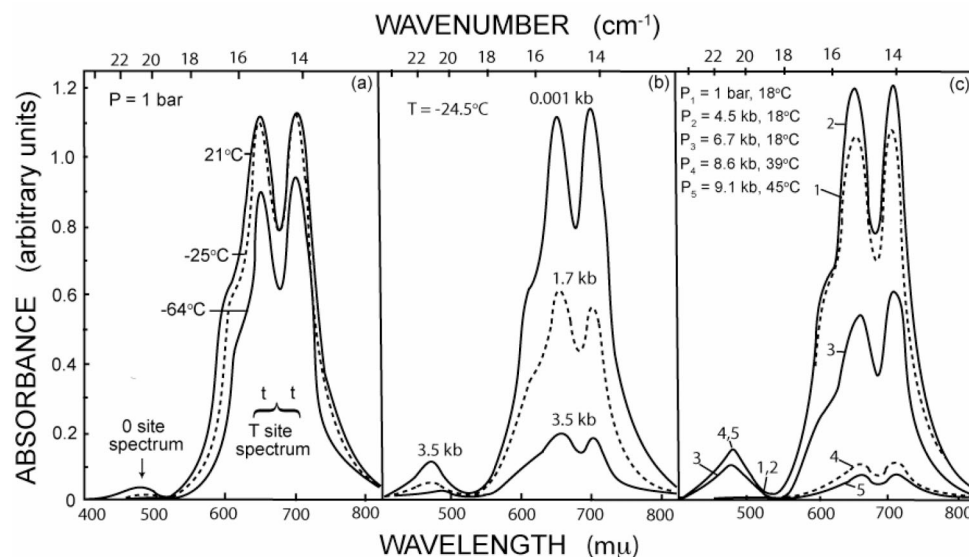
FIGURE 2. Electronic spectra (d–d transitions) of Ni(II) in a chloride environment both at 1 atm pressure and variable temperature down into the glass state (panel a) as a function of pressure up to 0.3 GPa at 24.5 °C and as a function of both up to 0.91 GPa, showing conversion from tetrahedral to octahedral coordination at high pressures and low temperatures. Reprinted with permission from ref 5. Copyright 1973 American Chemical Society.
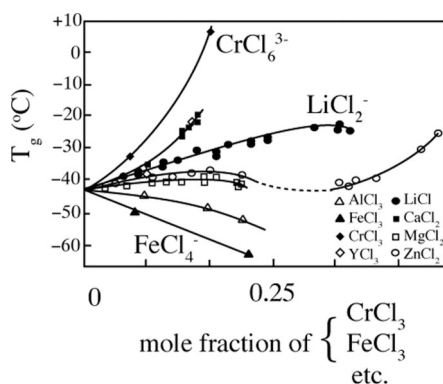

FIGURE 3. Variation of T_g of the simple chloride glass former α-methylpyridinium chloride on chloride complexation with various Lewis acids. Adapted from ref 6 by permission.

Ionicity of Ionic Liquids: Relation to Vapor Pressure and Conductivity

The "ionicity" of aprotic ionic liquids is the property that is responsible for their characteristic low vapor pressures. Low vapor pressure is the single most important property of this class of liquid, the property that, more than any other, is responsible for high level of interest in the field. However there is very little written about what exactly is involved in achieving high ionicity.[13] If the ions created in forming the ionic liquid were to remain locked together in pairs, the liquids would not be found to be of very low vapor pressure, and their conductivities would also be poor. They would just represent an unusual group of polar liquids. Indeed there are cases of aprotic ionic liquids in which for one reason or another the ions are largely paired up, and these are characterized by a high vapor pressure and a poor conductivity (see below). To obtain the low vapor pressures for which ionic liquids are generally reputed, the ions must distribute themselves in a uniform manner each ion surrounded by a symmetrical shell of
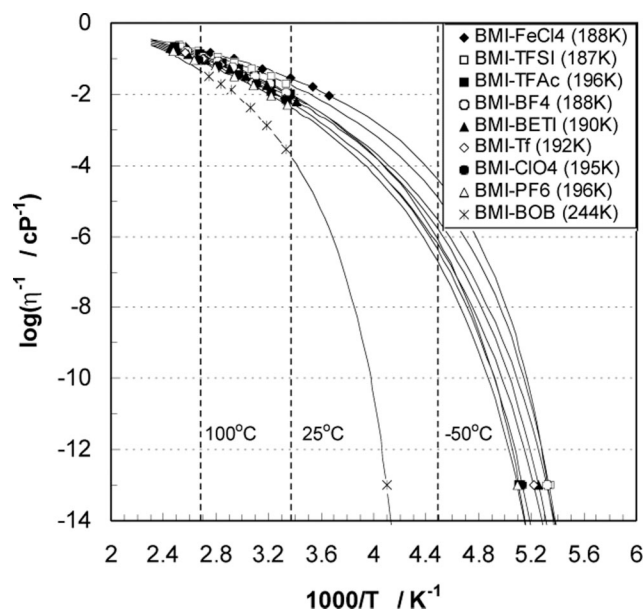

FIGURE 4. Fluidity data for a number of salts of the butylmethylimidzolium cation, showing that the tetrachloroferrate is more fluid than any of the fluorinated anion salts, in accord with its lowest T_g seen here (log $\eta^{-1} = 10^{-13}$) and in the Figure 6 legend. Reproduced with permission from ref 8. Copyright 2003 American Chemical Society.

the opposite charge. This is the distribution that minimizes the electrostatic potential energy, developing the liquid equivalent of the ionic crystal Madelung energy.[14] It is the difficulty of overcoming this electrostatic free energy to produce individual ion pairs that is responsible for the low vapor pressures of "good" ionic liquids.

An example of an ion-paired aprotic salt (unsymmetrical charge shell) is shown in Figure 5, which is a plot based on the classical concept, due to Walden, that ionic mobility is determined by the viscous friction of the liquid dragging on the ion as it attempts to move under the electrochemical force exerted by the DC electric field. This
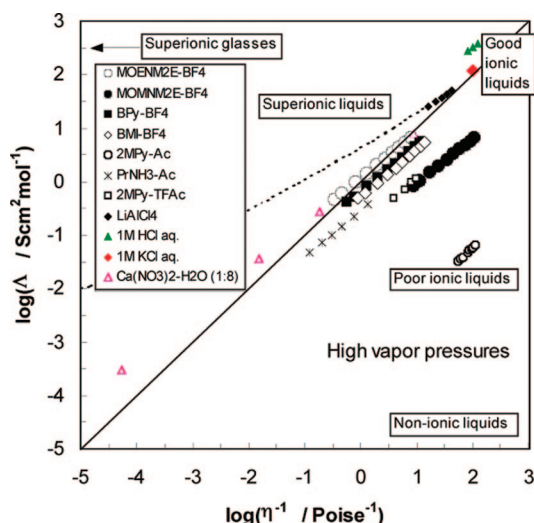
FIGURE 5. Walden Plot for ionic liquids and other molten salt and hydrate systems. Position of ideal line is fixed by data for KCl in 1 M aqueous solution. "Good" ionic liquids cluster on the ideal line. For exceptions, see text. Reprinted with permission from ref 15.
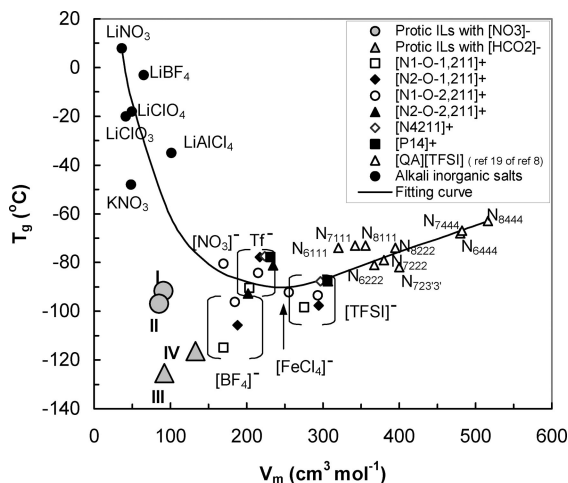

FIGURE 6. Glass transition temperatures of protic ILs in relation to the plot for aprotic salts of weakly polarizable anions from ref 8. Protic ILs are large shaded symbols (see ref 8 for details). Adapted from ref 8.

salt, methoxymethyl-dimethyl-ethyl-ammonium tetrafluoroborate (MOMNM$_2$E-BF$_4$ or [N$_{1-O-1,211}$][BF$_4$]) is seen, among the aprotic cases, to be that most clearly belonging to the "poor ionic liquids" domain[15] in Figure 5. It would have a high vapor pressure relative to others because it never developed the full Madelung potential. The precise reason why the cation and anion like to associate in this salt is not fully established, but it is probably due to the electron depletion of the methylene group between O and N$^+$ yielding acid protons that H-bond to BF$_4$fluorines in some lock-and-key manner.

The only "poorer" ionic liquid than [N$_{1-O-1,211}$][BF$_4$] in Figure 5 is a "protic" ionic liquid in which the drive to transfer the proton and create two ions is very weak. Protic ionic liquids as a class are given extensive discussion in a later section as they are among the most interesting and versatile of ionic liquids.

Figure 5 can be used to classify liquids between the groups "ionic" (whose members lie near the diagonal line), "subionic" (whose members lie below the line in the region labeled as "poor" ionic liquids), and superionic (whose members lie above the line by virtue of having some ionic species, usually small and low-charged, that can "slip through the cracks" in a nanoscopic sense and thus escape the full viscous drag of the surrounding medium).

Cohesive Energy of Ionic Liquids

The salts that develop the full Madelung potential are, by the above understanding, those that will have the largest cohesive energy (for given ionic sizes). Generally they will be the cases that have ions of comparable size and uniform shape so that they pack well and occupy a small volume. However salts that conform to this description will in general find it easy to crystallize into some high lattice energy structure and will have high melting points. They will therefore not be among the group known as "ionic liquids". To qualify as ionic liquids there must be some factor that lowers the lattice energy and thereby lowers the melting point. The "good" ionic liquids then must be those with some optimum departure from high symmetry, achieved by judicious (or serendipitous) choice of ion shape and interaction factors.

Those that achieve a sufficiently low melting point will then fail to crystallize and, on further cooling, will terminate in the glassy state. The temperature at which the liquid vitrifies, T_g, provides a second measure of the liquid cohesion. The plot is expected to have a minimum where decreasing Coulomb attractions balance increasing van der Waals attractions. Such a minimum is indeed found[8] in the vicinity of a volume that corresponds to a charge concentration of ~4 M (Figure 6).

The case of the "poor" ionic liquid [N$_{1-O-1,211}$][BF$_4$], in which the cations and anions are largely paired, is of interest in this connection. This aprotic ionic liquid was seen, in Figure 10 of ref 8 to have the lowest cohesion, by the T_g criterion, of any aprotic IL. This is fully consistent with its poorly developed Madelung potential. It is only underlain by the protic cases, I–IV, discussed below.

Aprotic Ionic Liquid Applications: Lithium Battery Electrolytes

Despite the interest widely expressed in ionic liquid-based lithium battery electrolytes, we omit reference to our recent studies in this area. This application is limited by a fundamental problem, discussed in ref 9 and illustrated in Figure 3, where it is seen that all small cations, including Li$^+$, get trapped as anionic complexes (by outcompeting the large solvent cations) and hence must lose mobility. This problem is reduced by use of fluorinated anions[9] but not overcome.

Protic Ionic Liquids: Properties and Applications

In contrast to the systems on which most of the work in the ionic liquid field has been performed (represented here by data in Figure 4), the protic ionic liquids are formed very simply by proton transfer from an inorganic acid to a Bronsted base. The base is usually organic in character, but there are also inorganic examples. The salt hydrazinium nitrate was reported in 1971 to have a melting point of only 70 °C,[16] and hydrazinium formate and hydrazinium acetate are both molten below 100 °C and can easily be studied through room temperature down to their glass transition temperatures.[16] The electrical conductance of hydrazinium formate at room temperature (measured in 1970 but only reported in the open literature in 2003[17]) is higher than that of any aprotic ionic liquid and is among the highest known. Many eutectic mixtures of ammonium salts are liquid below 100 °C, and these have recently been shown to be very interesting in application as fuel cell electrolytes,[18] as will be discussed further below. And of course there are the hydronium compounds such as hydronium triflate, which is congruently melting, T_m=35 °C, and has a very high electrical conductivity. Triflic acid and other superacids will presumably protonate many inorganic molecules that would not normally be considered as having cationic forms, so there are likely to be many additional inorganic protic ionic liquids recognized in the future. However the organic bases are far more versatile for protic ionic liquid formation.

There are organic bases not only from the primary, secondary or tertiary amines, but also with nitrogen atoms in heterocyclic rings (which may or may not be resonance stabilized).[19] There are also protonatable phosphorus analogs available, and sulfur-, selenium-, and iodine-based examples also exist.

An important aspect of protic ionic liquids is that the properties of the ionic liquid formed on proton transfer depend very strongly on the relative strengths of the acid and base between which the proton is transferred.[20] While the concentration of protonated species is always very high, of order 5–10 M in most cases, the properties may vary from strongly acidic to strongly basic in character, as is readily seen by simple tests with proton sensitive probes, such as the common indicator ions. For instance, a wide pH range litmus paper registers bright pink in contact with triethylammmonium triflate but dark blue in contact with triethylammonium acetate. The systematic and quantitative measurement of basicity in these solvent-free liquids is a recent achievement.

In order to assist the prediction of protic ionic liquid properties, the authors[20,21] have generalized the Gurney proton energy level diagram[22] not just to deal with proton transfers between acid and base species in an aqueous environment but, rather, to describe the energy changes when a proton moves between any proton donor and proton acceptor pair in the absence of any solvent at all. So far, for lack of alternatives, levels in the diagram relative to that of the H_3O^+/H_2O level have been based on the

Occupied	Vacant	pK$_a$	E (eV)
Acid Electrolytes			
HSbF$_6$	SbF$_6^-$		
HBOB	BOB$^-$		
HTFSI	TFSI$^-$		
HTf	Tf$^-$	-14	0.83
HSO$_3$F	SO$_3$F$^-$		
HClO$_4$	ClO$_4^-$	-10	0.59
H$_2$SO$_4$	HSO$_4^-$	-9	0.53
HPO$_2$F$_2$	PO$_2$F$_2^-$		
HNO$_3$	**NO$_3^-$**	**-1.30**	**0.08**
CH$_3$SO$_3$H	CH$_3$SO$_3^-$	-0.60	0.04
2-fluoropyridineH$^+$	2-fluoropyridine	-0.43	0.03
CF$_3$COOH	CF$_3$COO$^-$	-0.25	0.01
H$_3$O$^+$	H$_2$O	0	0
Neutral Electrolytes			
H$_3$PO$_4$	H$_2$PO$_4^-$	2.12	-0.13
1,2,4-1H-triazoleH$^+$	1,2,4-1H-triazole	3.00	-0.18
HF	F$^-$	3.20	-0.19
HCOOH	HCOO$^-$	3.75	-0.22
CH$_3$COOH	CH$_3$COO$^-$	4.75	-0.28
ImH$^+$	Im	6.99	-0.41
hydrazineH$^+$	hydrazine	7.96	-0.47
NH$_4^+$	NH$_3$	9.23	-0.55
EtNH$_3^+$	**EtNH$_2$**	**10.63**	-0.63
Bu$_2$NH$_2^+$	Bu$_2$NH	11.25	-0.67
H$_2$O	OH$^-$	14	-0.83
Basic Electrolytes			
NH$_3$	NH$_2^-$		
OH$^-$	O$_2^-$ (Na$^+$)	28	-1.66

FIGURE 7. The proton energy level diagram for predicting the ionicities of ionic liquids resulting from the falling of a proton from an occupied level (on an acid molecule) to a vacant level (on a basic molecule or on a divalent anion, in the latter case the countercation(s) must remain to balance the new anion charge). Reprinted with permission from ref 21. Copyright 2007 American Chemical Society.

known aqueous pK_a values, but this is of course only approximate because of the different dehydration energies of acid and base species in passing from aqueous to anhydrous systems. The approximate values will in time be replaced by energy levels based on NMR chemical shift studies[23] and other direct protic ionic liquids measurements, for instance, vapor pressure changes,[20] and particularly on voltages obtained from appropriate electrochemical measurements. The latter are just beginning.[24,25]

An example of the energy level diagram is provided in Figure 7.[21] It is constructed, following Gurney, by grouping acid and conjugate base forms of each molecule or ion together at a free energy level (in electronvolts) based on the arbitrary assignment of 0 eV to the couple H_3O^+/H_2O. The right-hand member of the couple is described as possessing an unoccupied quantized proton energy level, while the left-hand member has this level "occupied". The proton in the occupied level of any couple can "fall into" the vacant level of any couple lower on the diagram. When the occupied level of a couple lies on a neutral molecule, the fall of its proton to the unoccupied level of a couple at a lower level leaves behind a negatively charged species and creates a new positive species from the neutral
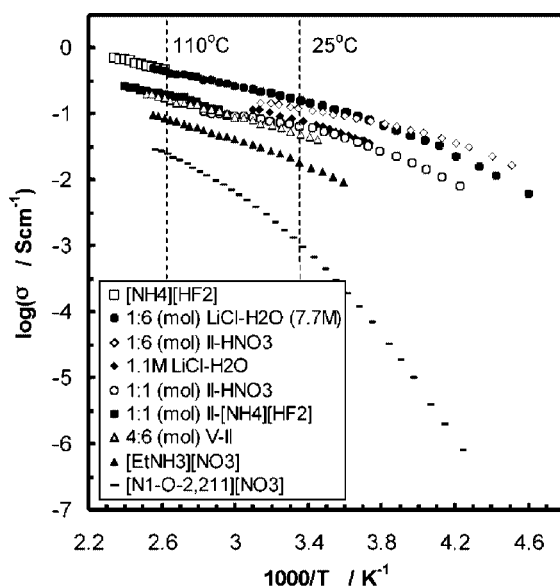
FIGURE 8. Conductivities of various protic ionic liquids (and one aprotic case, $[N_{1-0-2,211}][BF_4]$) compared with those of aqueous LiCl solutions to show how the aqueous solutions are no longer unique with respect to high ionic conductivity. II is dimethylammonium nitrate; V is methoxypropylammonium nitrate. Reprinted from ref 17 with permission of AAAS.

molecule into whose unoccupied proton level it fell, and an ionic liquid is created if the melting point of the product is below 100 °C, as is frequently the case. The relation between the level values is based on $E = -\Delta G/F = 2.303RT\Delta pK_a/F$.

We can now group the products of such proton transfers together into three protic electrolyte categories, acid, neutral, and basic. **Acid** protic electrolytes result when the proton falls from an occupied level on a superacid to a vacant level on a weak base, for example from triflic acid to fluoroaniline or to water, as in common aqueous acids. **Neutral** electrolytes arise when the proton falls from a moderately strong acid like nitric or methanesulfonic acid to a strong base like ethylamine or cyclopentylamine. Provided the proton falls across a gap of 0.7 eV or more, the electrolyte is a "good" ionic liquid, meaning the proton resides on the base for at least 99% of the time. Finally, **basic** electrolytes, for example, the product of proton transfer from a weak acid such as acetic acid to a base such as ethylamine, will give a poor ionic liquid. To obtain a truly basic ionic liquid, the cation of an initial proton transfer process yielding a product like Ethylammonium nitrate (EAN) must be combined with the product of second proton transfer process that yields a basic anion like OH^- or NH_2^- by some metathetical reaction, for example, $[CH_3CH_2NH_3^+][Cl^-] + NaOH \rightarrow [CH_3CH_2NH_3^+][OH^-] + NaCl$. Such compounds tend to be high melting and have been little explored to date. The properties of low melting liquids produced by reducing the charge density of the anion by complexation, for example, with a weak Lewis acid, such as $Al(OH)_3$, have yet to be explored.

The ionic conductances of some protic ionic liquids are shown in Figure 8 along with those of aqueous LiCl
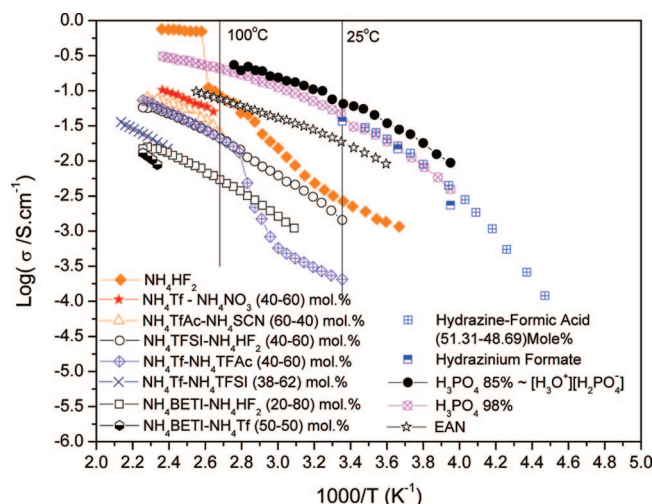

FIGURE 9. Arrhenius plot of the ionic conductivities of a collection of inorganic protic salts and salt mixtures (hydrazinium formate, ammonium bifluoride, and various ammonium salt mixtures). Comparison is made with ethylammonium nitrate and two phosphoric acids of different water content. Except for hydrazinium salts, the inorganic PILs are less highly conducting. High conductivity in solid state is shown for two cases.

to show that for some salts like dimethylammonium nitrate[17] the conductivities at ambient temperature can be as high as those found in aqueous solutions. The conductivity of an aprotic ionic liquid with low glass temperature, $[N_{1-0-2,211}][BF_4]$, is included for comparison.

Inorganic Protic Ionic Liquids

The smallest organic cation that can be obtained in an ionic liquid of the organic cation type is the methylammonium cation, $CH_3NH_3^+$. It is of interest to know whether, by passing to protic salts of the inorganic type, in which the cations are, for instance, ammonium or hydrazinium, even higher conductivities can be obtained. Hydrazinium nitrate and hydrazinium formate (having melting points below 100 °C)[16] were earlier cited as examples of inorganic ionic liquids, and the conductivity of hydrazinium formate was found to be extremely high,[18] though the finding remained unpublished until very recently. The conductivity of ammonium bifluoride, although not strictly an IL (having a melting point of 125 °C), is even higher.[17] Now we can add the conductivities of a number of ammonium salt mixtures, whose eutectic temperatures fall well in the IL range, to the collection of inorganic ionic liquids. The conductivity data for these systems[18] are shown in Figure 9.

In Figure 9, the conductivities, while indeed very high, do not reach the values of the best organic cation ILs except in the case of the hydrazinium formate. The case of ammonium bifluoride is exceptional, and it is possible that this unusual liquid, extensively used as a cleaning and a fluorinating agent in inorganic fluoride chemistry[26] may be a "dry" proton conductor.
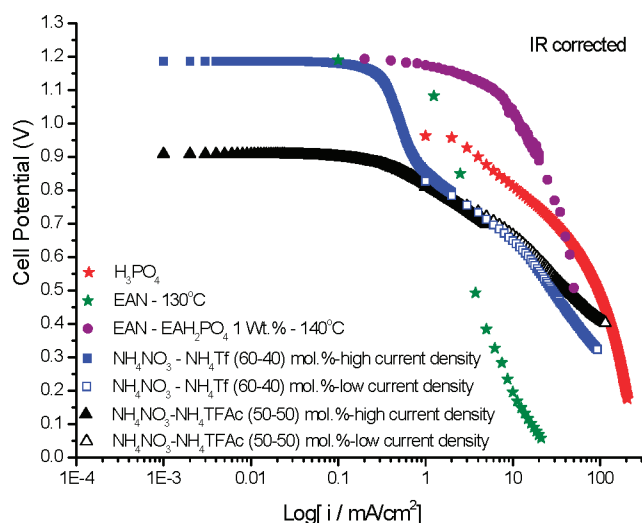
FIGURE 10. IR-corrected polarization curves for hydrogen/oxygen fuel cells utilizing inorganic and organic cation ionic liquid electrolytes. Reproduced from ref 18 by permission.

Protic Ionic Liquids As Fuel Cell Electrolytes

It is astonishing that protic ionic liquids had been known for nearly a century before it was realized[27,28] that they could serve as the proton carriers in fuel cell electrolytes. In fact, they can serve very well in this role and can provide electrolytes of a type that are simply not available in systems in which water acts as acid or base in the proton transfer process.

It is even more astonishing that until 2006 it had not been realized that mixtures of **inorganic** salts (namely, the ammonium salts) can be used as protic electrolytes for fuel cells running above 80 °C (hydrazinium salts could be used to much lower temperatures). Applied as fuel cell electrolytes, the ammonium salts give more stable performance than electrolytes containing organic cations. The IR-corrected polarization curves for some inorganic electrolyte fuel cells are shown in Figure 10, using the logarithmic current ("Tafel plot") form. The plateau current at the theoretical voltage can now be extended out to 50 mA·cm^{-2} in some inorganic systems to be described in future articles, beyond the previously recognized limits. The increase in efficiency relative to the phosphoric acid cell is about 20%, and the implied reduction in generated heat may be very important in some applications, which do not require high power.

While the ionic liquids offer the possibility of higher efficiency cells, the phosphoric acid (PA) cell has a significant advantage in kinetics. The kinetic advantage lies in the higher conductivity of the phosphoric acid, which is a molecular liquid that exhibits not only considerable autoionization but also "dry" proton mobility. This superprotonic component, which is illustrated in Figure 11, is unfortunately not present in the protic ionic liquids, which mostly lie on or below the "ideal" Walden line.[8] It may be necessary to compromise on power output for the sake of energy efficiency, though the NH$_4$HF$_2$ data in Figure 9 suggest that breakthroughs may eventuate.

In an initial report on the relation of fuel cell voltage output to other properties of the PILs,[18] we noted a
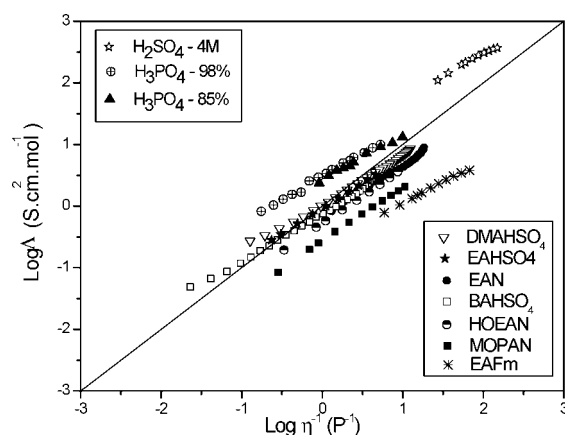

FIGURE 11. Walden plot showing the behavior of equivalent conductivity expected from precise correlation with liquid viscosity solid line, with examples of subionic behavior in some protic salt cases and superprotonic behavior in some acid + water systems. Reprinted with permission from ref 21. Copyright 2007 American Chemical Society.

relation between the output voltage and the difference in pK_a values for the acid and base components of the electrolyte. The voltage increased strongly with increasing ΔpK_a and reached the theoretical value when the ΔpK_a value for the electrolyte reached about 14. There is now an urgent need to develop direct measures of the free energy of proton transfer for the anhydrous case.

In Situ Measures of Proton Transfer Energetics and Relative Proton Activities in Ionic Liquids

Two steps have now been taken toward direct proton transfer energy characterization. The first[23] has been to study the NMR proton chemical shift for the proton that has been transferred to the base nitrogen but is still being counterattracted by the conjugate base of the acid from which it came. The stronger the "pull" from the conjugate base (which means the smaller the free energy of transfer), the more deshielded will be the N–H proton. The more deshielded the proton, the further downfield its resonance frequency will lie relative to a standard reference, for example, C(CH$_3$)$_4$. Thus the N–H chemical shift (δN–H) can serve as an in situ probe of the proton transfer energy. We find immediately that it does not enjoy a linear relation with the value of ΔpK_a but rather gives a relationship similar to that between the fuel cell open circuit voltage (OCV) and the ΔpK_a value.[18] The second step has been to develop a method of measuring directly the voltage necessary to displace a proton from its normal site on a nitrogen onto the anion from which it originally came. This will be described elsewhere.[29] A preliminary correlation of voltage output from a modified glass electrode with the N–H proton chemical shift discussed in the next section, has been given in an abstract for the Ionic Liquids meeting (COIL 2, Yokohoma, July 2007). These direct measures have already found application in another recently developing application of ionic liquids, namely, the stabilization of biomolecules discussed in the next section.
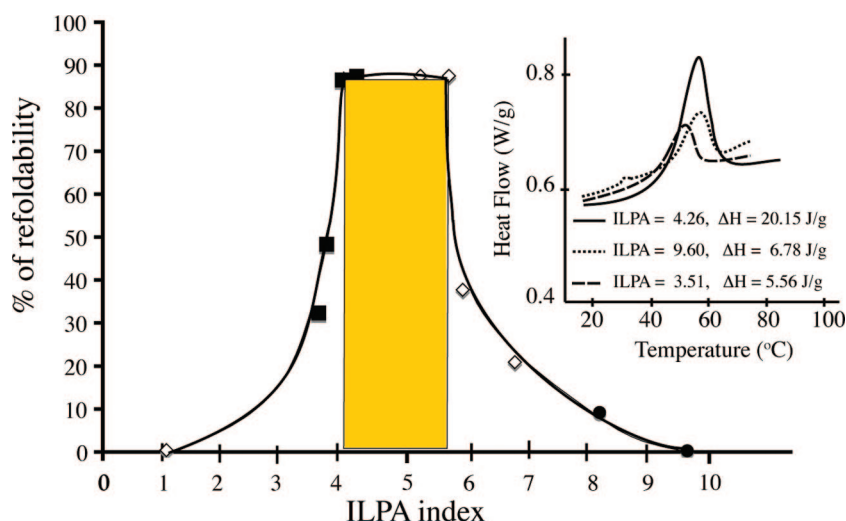
FIGURE 12. Refolding fraction (defined by the ratio of areas under the DSC unfolding endotherms of second to first upscans) as function of PA represented by the ILPA index (Ionic Liquid Proton Activity) which is a substitute for pH. The ILPA value is determined using a modified glass electrode, to be described elsewhere. The values depend on the reference electrode and liquid junction potential corrections, so they are only provisional in this figure. It correlates linearly with the N–H proton chemical shift δ(N–H). Insert shows the unfolding endotherms in the most stable domain compared with those on either side. Closed markers are single component solutions and open diamonds are 1:1 binary mixtures of EAN–TEATf, EAN–TEATfAc, and EAN–EAFm.

Proton Activity and Protein Stabilization in PILs

An exciting new role for ionic liquids may lie in the storage and manipulation of sensitive biomolecules. Fujita et al.[30] have recently reported that the protein cytochrome *c* is remarkably stablilized in solution in a nontoxic dihydrogen phosphate IL, and we have found[31] that lysozyme in 200 mg/mL concentration is still folded after 3 years in ambient solutions with large ethylammonium nitrate concentrations. The source and full extent of this stability is not yet properly understood.

It is well-known from standard biological concentration solution studies that each protein has pH range in which its native state is most preferred and that deviations from that pH range can affect its folding energy and its stability against such undesirable behavior as aggregation, and recently, fibrillization. It might be expected that the proton activity of the solvent will exert a strong effect on the stability of proteins in the ionic liquid protective solution, and this is verified by our findings,[32] which are shown in Figure 12. In Figure 12, the proton activity is represented by the δ(N–H) while, for stability on the vertical axis, we use a refoldability index pending the necessary long-term assessments.

The refoldability index is the percentage of the initial enthalpy of unfolding obtained after lowering the temperature to allow thermally denatured molecules to refold and then remeasuring the unfolding enthalpy. The difference between the two is a measure of the fraction of the protein lost to the aggregation process and is found to be 3%. The stability index is then given by the ratio (second unfolding enthalpy)/(first unfolding enthalpy) and is 0.97, or 97%, under favorable circumstances. The "% refoldability" for hen egg lysozyme is shown as a function of the proton activity measured electrochemically with a modified glass electrode to be described elsewhere. The

ouput voltage of this device is used to define an "ILPA" index which correlates linearly with the N–H chemical shift (δ(N–H)) determined for the solution in which the lysozyme was dissolved, in Figure 12. The presence of an ILPA range equivalent to about 2 pH units, in which the same high refoldability index is obtained is quite striking. The refoldability index varies as a function of water content at constant ionic liquid content. But when the δ(N–H) of the solution is measured, it is found that the δ(N–H) has also changed with water content, and it is evidently only the proton activity that is important. The solution in which the 3 years stability was recorded[31] happened to have been formulated near the center of the maximum stability zone of Figure 12 for lysozyme.

Different proteins have different favorable proton activity stability ranges. We hope to establish these optimum conditions for many normally fragile biomolecules so that they can be preserved indefinitely at ambient temperatures, thereby opening the door to unrefrigerated shipping and storage of drugs and other biologically important materials.

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Proton activity in ionic liquids: The ILPA index and its application in optimizing fuel cell efficiency, protein stability, and large molecule solubility.

C.A. Angell[1], N. Byrne[1], J-P. Belieres[1],)

[1] Dept of Chemistry and Biochemistry, Arizona State Univ., Tempe, AZ 85287, USA.

$[CH_3CH_2NH_3^+][NO_3^-]$, called EAN, $[H_3O^+][CH_3SO_3^-]$, 1:1$NH_4NO_3.NH_4SCN$, are all liquid below 100ºC, and consist only of ions, hence are "ionic liquids". They are of the protic class, organic and inorganic. Every positive ion is protonated and their concentration is of order V_M^{-1}, (5-10M). Despite such similar concentrations, the differences in proton activities can be many orders of magnitude due to the different proton "energy gaps", and thus proton bindings on the base[1].

We show that H^+ activities, which had not been quantified before our work reported at this meeting (see also Byrne, and Belieres, abstracts), can control the energy conversion efficiency of fuel cells in which they are the electrolytes, the stability of folded hydrated proteins in liquid storage systems, and presumably the kinetics of many chemical reactions and other processes. In the case of PILs with nitrogenic proton acceptor sites, an internal measure of the protonic state is available through the N-H proton magnetic resonance PMR chemical shift [2]. The more basic the PIL, the greater the downfield proton shift (opposite to the usual aqueous solution experience).

An "apparent pH" can be measured with a standard solution pH meter (after large calibration voltages are applied) but the correlation with the N-H PMR chemical shift is erratic and saturates at ~pH 7. Here we report our development of a device [3] that gives voltage output of ~zero for the "neutral" PILs (EAN and TEAMS), positive voltages for more acid, and negative voltages for more basic cases, and a

linear, non-saturating, relation to the N-H proton chemical shift [2], Fig. 1. We use these voltages to define an Ionic Liquid Proton Activity (ILPA) index. Since the device also measures standard solutions we assign ILPA values to correspond with aqueous buffer pH values. We relate the voltage output of the new device (an ILPA meter) to energy levels in the Gurney diagram for PILS [1] that were previously [1] based on pK_a values from aqueous solutions for want of a better metric. Then we use the quantified H^+ energy levels to correlate/predict other IL applications.
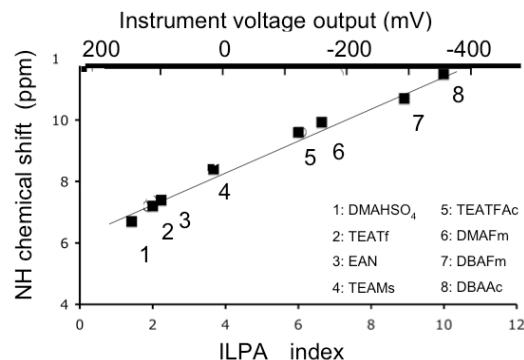

Figure 1: Linear variation of the proton activity (ILPA index) with N-H proton chemical shift (NMR) for 8 protic ILs.

Since the ILPA changes rapidly near PIL stoichiometry, buffering is desirable. We demonstrate various buffers and the "tuning" of H^+ activity to desired values. Aprotic ILs (with trace H_2O?) are base-shifted relative to PILs of like anions.

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ON THE RELATION OF "DRY" PROTON TO "FAST" LI$^+$ CONDUCTIVITY IN CRYSTALLINE, GLASSY, AND POLYMER SOLID ELECTROLYTES

C. Austen Angell

Dept. of Chemistry, Arizona State University, Tempe, AZ 85287, USA, and
Dept. of Chemistry, Sydney University, NSW 2066, Australia

Email: austenangell@gmail.com

Keywords: protonic conductivity, superionics, decoupling, lithium batteries, fuel cells

Introduction

Electrolyte requirements for lithium batteries and fuel cells have evolved in parallel, along essentially independent paths. This is a little surprising in view of the fact that both the proton and the Li$^+$ cation are small, high charge intensity, entities each with Lewis acid properties. In this lecture we review the recent progress in harnessing each type of electrolyte for applications, and try to emphasize the points of overlap on the one hand and difference between them on the other.

In each case there is, of course, great interest in finding conditions for maximum decoupling of the entities H$^+$ and Li$^+$ from their environments because of the advantages with respect to cell polarization that such "single ion conductors" must have. There are more examples of Li$^+$ ion decoupling than there are of H$^+$ ion decoupling, the term Grotthus mechanism commonly being used to describe the phenomenon in the latter case.

Coupling and Decoupling.

To quantify the (favorable) decouplings and (unfavorable) couplings, we use either of two common diagrams, the Walden plot and the T$_g$-scaled Arrhenius plot [1]. The first of these diagrams, shown in Fig. 1(a), is usually only employed to discuss the high conductivity end of the overall phenomenology, while the second is best suited for discussion of glasses and polymers. Neither is satisfactory for the discussion of plastic crystals [3-5], which do not have liquid-like viscosities. We discuss new cases of this sort of conductor. Also, care must be taken in use of the Walden plot in the case of polymer electrolytes because in these cases there is a built-in decoupling of the conductivity from fluidity due to the "polymer effect" on the viscosity [6]. But most polymers are very poor conductors at their T$_g$s, so Fig. 1(b) is not so useful either. We discuss polymer-in-salt and polymer-in-ionic liquid cases, which avoid such T$_g$ control.

The decoupling of Li$^+$ from the glass or polymer structure, is the equivalent of "dry" proton conductivity. It is a more common phenomenon. The decoupling can be quantified by the excess of equivalent conductivity Λ over the Walden value, or by the ratio of conductivity relaxation time to the structural relaxation time. Data are shown for the cases of LiAlCl$_4$, H$_3$PO$_4$ and H$_2$SO$_4$ and some ionic liquids, for which both Λ and η data are available. More common for Li are conductivity data below T$_g$ [2,7]. At T$_g$, the structural relaxation time has a standard value (100s) and the relaxation time ratio at T$_g$
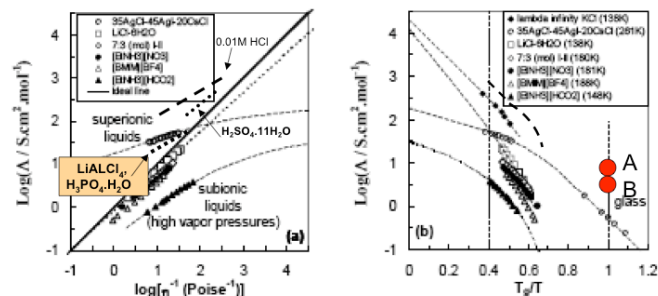

Figure 1(a). Walden classification plot exhibiting, ideal Walden behavior (diagonal), subionic behavior (below the diagonal) and superionic (or superprotonic) behavior (above the diagonal). The abscissa limiting value of 4.5 corresponds to the infinite temperature fluidity with shear relaxation time equal to the inverse lattice vibration frequency{x} (b). T$_g$-scaled Arrhenius representation of the same conductivity data, displaying the decoupling in the solid by the L value at T$_g$ where the structural relaxation time is believed to be 100s. Points A and B are for the maximally decoupled Ag$^+$ and Li$^+$ glasses of Martin and coworkers [2] viz. A: 0.3 AgI + 0.7(Ag$_2$S$_{50}$·[0.67GeS$_2$:0.33B$_2$O$_3$]$_{50}$), and B: 0.7(Li$_2$S)0.3(B$_2$S$_3$) at their respective T$_g$s.

then becomes a material characterization property [7], the decoupling index.

In the subionic domain of Fig. 1(a), incomplete proton transfer causes ion pairing and hence diffusion without conductivity. *What is the equivalent of this domain when it is the lithium ion that is in focus?* In one instance it will be molecular salt cases like that of the fluoro-salt Li bisperfluoropinocolatoborate, which is low melting and distillable [8]. In others, it will be systems in which the lithium ion is captured by Lewis base anions that convert it to a sort of complex anion, e.g. LiCl$_2^-$ [9]. Then it cannot move freely towards the cathode, and in extreme cases, could acquire a negative transport number. As was found in early work in this area [10], this "Li$^+$ trapping" is a fundamental problem for current efforts to make lithium salt polymer electrolytes using "ionic liquid" solutions (which are then incorporated into polymer hosts to make "solid electrolytes").

All these factors will be incorporated into an overview of the field and a prospectus for future progress.

References [1-10] are provided in this abstract on the author's website: www.public.asu.edu/~caangell/

1. **"Protic Salt Polymer Membranes: Water-Free Proton-Conducting Membranes",** Southeast Regional Meeting American Chemical Society (SERMACS), Greenville, SC, October 26, 2007.

Don Gervasio
Arizona State University

Fuel cells generate significant interest, because they offer more efficient power generation than combustion engines while avoiding pollutants like carbon monoxide, nitrogen oxides and ozone.

A polymer electrolyte membrane (PEM) is favored in fuel cells. A PEM is a solid electrolyte, which is immobile, which maintains cell structural integrity. This maintains electrode separation and prevents ion leakage to prevent internal shorts, which is especially important for using fuel cells in portable applications, like, automobiles.

The present state of the art PEM is made of a perfluorinated alkylsulfonic acid ionomer, Nafion. Nafion and similar sulfonated membranes need to be highly hydrated and operate at near room (< 80 ^{o}C), which result in bulky inefficient fuel cells due to cumbersome water management ancillaries and overly large waste heat radiators. New protic salt polymer membranes, which operate at higher temperatures and conduct protons in the absence of water practically eliminate the bulk and inefficiencies of heat and water management devices needed to operate the fuel cell with Nafion PEM. This can greatly reduce overall fuel cell size, weight, complexity and cost.

Protic salt electrolytes are formed by proton transfer between an equimolar mixture of a Bronsted acid and a Bronsted base. For example, when ethyl ammine is combined with nitric acid, ethyl ammonium nitrate (EAN) forms. At ASU, it was discovered that when the pKa of the acid and base moieties in the salt differ by ~ 14, as they do in EAN, then a neat liquid protic salt electrolyte forms, which is a water-free proton conductor from room temperature to temperatures as high as 200°C. A hydrogen-oxygen fuel cell gives 20% higher efficiency operation with EAN instead of with an aqueous electrolyte, like phosphoric acid. Accordingly membranes filled with protic ionic liquids and membranes with covalently attached protic salt moieties are promising candidates for use in high-temperature (120°C) low-humidity polymer-electrolyte-fuel-cell (PEFC) power sources for portable applications.

Proton electrolyte membranes based on protic salts have promise not just in more efficient practical fuel cells but also in more efficient electrochemical synthesis, e.g., for hydrogen electrolyzers. Fuel cell and electrolyzers have key roles in making the concept of a clean and renewable "hydrogen economy" a reality.

The fundamentals and materials science for making PEMs based on protic salt complexes will be presented.

This is the "abstract" from our group's invited presentation at the Pira Conference on Ionic Liquids, Orlando, Florida, December 2006.

1. Ionic liquids and fuel cell membranes: a new generation of polymer electrolyte fuel cell membranes using the anhydrous protic ionic liquid principle, (Presented by J.-P. Belieres).
Jean-Philippe Belieres, Xiao-Guang Sun, Don Gervasio and C. Austen Angell,
PIRA conference on Ionic Liquids, Orlando, FL, December 11-13, 2006

Ionic liquids and fuel cell membranes: a new generation of polymer electrolyte fuel cell membranes using the anhydrous protic ionic liquid principle

- Fuel cells and the Hydrogen economy
- Optimizing a protic ionic liquid (PIL) as a fuel cell electrolyte
- Advantages of water free proton conduction above and below 100° C
- Two approaches to Fuel Cell Membranes
    - Now: PIL-swollen polymer target conductivity of 100 mS/cm at 100°C
    - The future: ions immobilized in membranes with the same conductivity?

Dr Dominic Gervasio, Associate Professor Research, ARIZONA STATE UNIVERSITY, US

Protic ionic liquids and the PEM fuel cell

Jean-Philippe Belieres[1], Nolene Byrne[1], Don Gervasio[2] and C. Austen Angell[1]

[1]Arizona State University, Chemistry. and Biochemistry Dpt., Tempe, AZ 85287-1604, USA

[2]Center for Applied Nano-Bioscience, Tempe, AZ 85287-5101, USA

C. Austen Angell, caa@asu.edu

The need for cleaner alternative energy sources combined with the high energy density provided by fuel cells play an important role in the renewed interest in the fuel cell technology. The problems of electrode kinetics, water management and cost, would be reduced if an inexpensive high temperature electrolyte permeable only to protons could be used. We have developed a promising class of electrolytes, neat proton transfer salts with "tailored" proton transfer energies [1], which in simple H_2/O_2 "bubbler" fuel cells yield better performance than the same cell with the 85% H_3PO_4 electrolyte [2]. Made by neutralizing a Bronsted acid with a Bronsted base of suitable pK_a value, these protic ILs may have either inorganic [3] or organic [1] cations, and may be neutral, acid or basic, depending mainly on the anion. The proton activity is highly variable, depending on free energy of proton transfer. It may now be determined using an "Ionic Liquid Proton Activity" (ILPA) meter (plenary C. A. Angell).
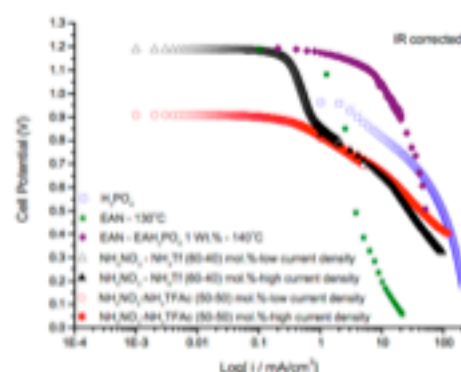

Fig.1 H_2/O_2 fuel cell using ETEK electrodes (Pt 0.5 mg/cm^2) with binary mixtures, EAN and 85% aqueous H_3PO_4 as the electrolyte at 140°C. (From Ref. 3, by permission).

PILs not only transport protons but also tend to be more fluid and conductive than the aprotic ILS [4]. Their use as fuel cell electrolytes was first reported by Susan et al. [5], though the use of imidazole and related molecules as proton carriers in polymeric membrane electrolytes began earlier [6]. In this laboratory we have shown that when ethylammonium nitrate or other ILPA-selected PILs are used as electrolyte, there is almost no polarization at the oxygen electrode.

With organic cations, the cell lifetime is usually limited, probably because of C–H bond cleavage in the presence of the platinum catalyst. But we now report that low-melting *inorganic* salts with protonated cations (e.g. ammonium) also act as electrolytes in fuel cells operating in the temperature range 100-200°C and, even with un-optimized electrodes, cell performance is comparable to that of the phosphoric acid fuel cell operating with optimized (ETEK) electrodes in the same temperature range [3], see Fig. 1 and there is no need for humidification or pressure to sustain performance. The melting points of binary eutectics are low and their conductivities are very high compared to those of most aprotic ionic liquids. At 150°C, the conductivity can reach values comparable to those of aqueous solutions [4]. We will show PEM fuel cell performances using these protic ionic liquids.

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Binary inorganic salt mixtures as high conductivity liquid electrolytes for high temperature fuel cells.
J.-P. Belieres[*], N. Byrne[*], X.-G. Sun[*], L. Holmes[*], G. Tucker[*], D. Gervasio[#], J. Yarger[*] and C. A. Angell[*]
*Chemistry and Biochemistry Department
#Applied NanoBioScience Center
Arizona State University, Tempe AZ 85287

The need for alternative energy sources and the high energy density provided by fuel cells relative to that of other portable power systems play an important role in the renewed interest in the fuel cell technology[1,2]. The persistent problems (i) electrode kinetics, (ii) electrolyte water management and (iii) cost, would be diminished if an inexpensive high temperature electrolyte permeable only to protons could be found[3-5]. We have developed a promising class of electrolytes, neat proton transfer salts with "tailored" proton transfer energies, which seem to yield ideal (theoretical) open circuit voltages in simple H_2/O_2 fuel cells. Made by neutralizing a Bronsted acid with an equimolar Bronsted base of chosen pK_a value (to yield a free energy change of 0.7-1.0 eV), these protic ILs can be neutral and need no solvent to transport protons between electrodes. Relative to water, they are involatile[6].

Interest has turned to these PILs because they not only transport protons but also tend to be more fluid than the aprotic cases, hence more conductive[7]. The use of solvent-free ionic liquids as fuel cell electrolytes was first reported by Susan et al.[8], though the use of imidazole and related molecules as proton carriers in polymeric membrane electrolytes had begun earlier[9]. In this laboratory we have shown that when ethylammonium nitrate or other carefully chosen PILs are used as the electrolyte[6,10], there is almost no polarization at the oxygen electrode[5,11]. The result is that the cell voltage approaches and sometimes exceeds the theoretical 150°C value of 1.15 V (for all participants in standard states).

With organic cations, the cell lifetime is usually limited, probably because of C–H bond cleavage in the presence of the platinum catalyst. But we now report that low-melting inorganic salts with protonated cations (e.g. ammonium) also act as electrolytes in fuel cells operating in the temperature range 100–200°C and, even with unoptimized electrodes, cell performance is comparable to that of the phosphoric acid fuel cell operating with optimized electrodes in the same temperature range[12]. Indeed, open circuit voltages, and efficiencies at low current densities, can be much better and there is no need for humidification or pressure to sustain performance. The conductivities of binary eutectic melts are very high compared to those of most aprotic ionic liquids. Fig. 1 presents data in Arrhenius plot form, making comparison with that of ethylammonium nitrate presented in earlier work[7]. At 150°C, the conductivity can reach values comparable to those of aqueous solutions[7].

Using E-TEK electrodes and an in-house Teflon

equimolar $NH_4NO_3 + NH_4TFAc$ electrolyte proves to be one of the most stable of all electrolytes tested, yielding invariant potential at fixed load, day after day of cell use. The cell using 60:40 NH_4NO_3:NH_4Tf yields a very high open circuit voltage. The large current densities often reported for cells using 100 micron or less thick membranes[11], are not to be expected in our work, because (i) our cell was designed with a 1/8" thick electrolyte compartment gap between electrodes to permit easy exchange of electrolytes and (ii) the ETEK electrodes were optimally designed for aqueous H_3PO_4 electrolyte.
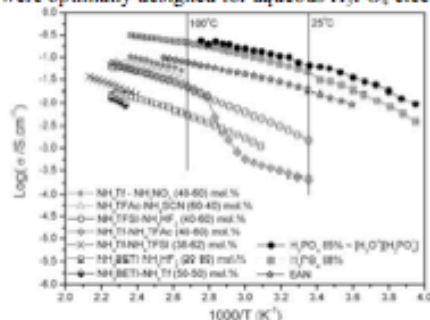

Fig.1: Arrhenius plot of conductivities of ammonium salt mixtures. Comparison is made with EAN and H_3PO_4 of different water content. (From Ref. 12, by permission).
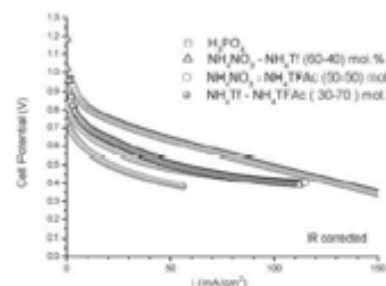

Fig.2: H_2/O_2 fuel cell using ETEK electrodes (Pt 0.5 mg/cm^2) with binary mixtures and 85% aqueous H_3PO_4 as the electrolyte at 140°C. (From Ref. 12, by permission).

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